Gianluca Stefanucci

Quantum Mechanics for Material Science

An Introduction

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To my wife Marina

Preface

This book arises from the lecture notes of the course "Elements of Theoretical Physics," part of the "Materials Science" degree at the University of Rome Tor Vergata, which I taught between the years 2017 and 2023. They contain an introduction to quantum mechanics, surgically tailored to provide students with essential concepts and tools for subsequent courses without sacrificing the completeness of the treatment. At the end of each chapter, the reader can find a series of solved exercises and other exercises, useful both for absorbing theoretical concepts and for applying the mathematical tools explained.

Understanding the content of this book, and more generally, quantum mechanics, requires some familiarity with certain mathematical concepts assimilated in previous courses. For accuracy, knowledge of

- limits, derivatives and integrals;
- Taylor series;
- vector spaces, linear operators and Dirac notation;
- hermitian and unitary operators, eigenvectors and eigenkets;
- function of operators—spectral representation.

I would like to first thank Prof. Enrico Perfetto, with whom I have had several discussions, for conducting the exercises of the course and proposing some of the exercises included in this book. I also thank the students who have followed over the years for stimulating me to refine the presentation of various topics year after year. Any errors that may be present are the sole responsibility of the undersigned.

Rome, Italy Gianluca Stefanucci

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Chapter 1
The Fundamental Concepts of Quantum Mechanics

1.1 The Need to Abandon Classical Physics

To understand the problems of classical physics in describing the microscopic world, let's start with a concrete example. Let's consider the hydrogen molecule ion, H_2^+. This ion consists of two protons, located at a distance of about 10^{-10} m, and one electron. The mass of the protons is $m_p = 1.67 \times 10^{-27}$ Kg, which is approximately 1800 times greater than the mass of the electron, $m_e = 9.11 \times 10^{-31}$ Kg. We can then treat the two protons as fixed in their equilibrium positions, denoted by R_1 and R_2, while the electron is free to move around them. The electron is, of course, attracted to the protons due to the Coulomb force, and if the electron is at position r, its potential energy is

$$V(r) = -\frac{e^2}{|r - R_1|} - \frac{e^2}{|r - R_2|} \tag{1.1}$$

with $e = 1.6 \times 10^{-19}$C being the magnitude of the electric charge. Choosing the coordinate origin equidistant from both protons, the potential energy of Eq. (1.1) is illustrated in Fig. 1.1 and takes the form of a double well.

Classically, if the electron is located at r and has momentum p, its energy E is the sum of the kinetic and potential energies, namely $E = \frac{p^2}{2m} + V(r)$. Thus, the lowest energy state corresponds to an electron with zero momentum (minimizing the kinetic energy $\frac{p^2}{2m}$) positioned at the center of either the first or second well (minimizing the potential energy). This is the classical prediction. However, to verify the correctness of this prediction, we must perform the experiment and measure the position and momentum of the electron.

In the experiment, we first bring a gas of H_2^+ molecules into contact with a source at absolute zero temperature to minimize the energy of each molecule. We then proceed to measure the position r and energy E of the electron in each molecule

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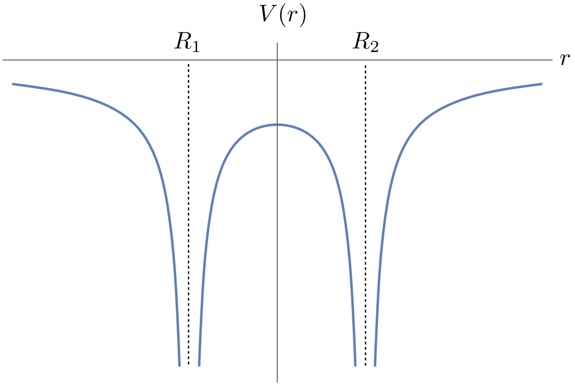
Fig. 1.1 Profile of the potential energy of an electron immersed in the electric field generated by two protons placed at R_1 and R_2



(from which we can extract the momentum as $p = \sqrt{2m[E - V(r)]}$). As we see, the result of the experiment does not confirm the classical prediction. It is going to be a real puzzle, but we will find a way out.

Let's start by measuring the position of the electron for a large number of molecules. Clearly, it is not be possible to measure the position with infinite precision, but we can determine whether the electron is located in a small vicinity of R_1 or R_2. In fact, this is precisely what experimentally happens; the electron is always found in the vicinity of one of the two wells, in accordance with classical physics. *Immediately after measuring the position*, we proceed to measure the energy, molecule by molecule, once again. And here is where the puzzle begins. Regardless of the just-measured position, the energy always turns out to be higher than the minimum predicted by classical physics. Even more surprisingly, although all molecules are in the same condition, for some of them, the measured energy is a certain value E_a, while for others, it is a different value $E_b \neq E_a$. The probability of measuring E_a is roughly the same as measuring E_b, and both are slightly less than 0.5:

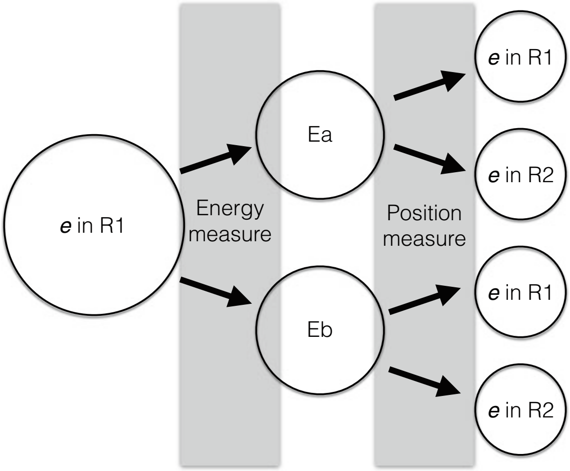
$$P(E_a) \simeq P(E_b) \simeq 0.5 \tag{1.2}$$

All other measured energy values are larger than both E_a and E_b and are neglected here since the probability of measuring them is extremely small. There are facts; nature indeed behave this way, take it or leave it. If we take it then fundamental questions inevitably arise:

Why is the measured energy always greater than the minimum predicted by classical physics? And why is it not always the same? How do we know whether we will measure E_a or E_b? From these data, it seems impossible to simultaneously know the position and energy, or equivalently, the position and momentum. *If we know the position, there is uncertainty in the energy, and therefore in the momentum.*

The peculiarities of the microscopic world do not end here. Let's take all those molecules that provided us with energy E_a and orient them in such a way that the previously measured position of the electron is to the left of the origin, thus in the

Fig. 1.2 An electron measured at R_1 has equal probabilities of having energy E_a or E_b. After measuring the energy, the same electron has equal probabilities of being measured at R_1 or R_2



vicinity of R_1. Well, let's now measure the position of the electron again. What we find is unbelievable. In half of these molecules, the electron is still in the vicinity of R_1, while in the other half, it is in the vicinity of R_2! So, now that we know the energy with certainty, we no longer know the position with certainty. If we had chosen the set of molecules with energy E_b, we would have obtained the same result. We must conclude that *if we know the energy, there is uncertainty in the position*. In Fig. 1.2, we summarize graphically the results obtained experimentally. It is evident that classical physics cannot help us unravel this entanglement.

As if that weren't enough, there is another peculiarity. Let's take the set of molecules on which we measured energy E_a. For each of them, after the measurement, we wait for a time t and measure the energy again. What we find is that for all molecules, the energy is still E_a. If we had performed the same experiment for the molecules with energy E_b, we would have found the same result, i.e., after a time t, we would always measure E_b. However, things change when we measure the position twice at a time interval. Let's take the set of molecules on which we measured the position and orient them so that, for all of them, the electron is located in the vicinity of R_1. If we now wait for a time t and measure the position of the electron again, we find that the electron is in the vicinity of R_1 for some molecules and in the vicinity of R_2 for the remaining molecules! To be more precise, what we find is that the probability of remeasuring the electron in the vicinity of R_1 after a time t oscillates over time as follows

$$P(R_1) = 0.5 \times [1 + \cos(\Omega t)] \tag{1.3}$$

where

$$\Omega = \frac{E_b - E_a}{\hbar} \tag{1.4}$$

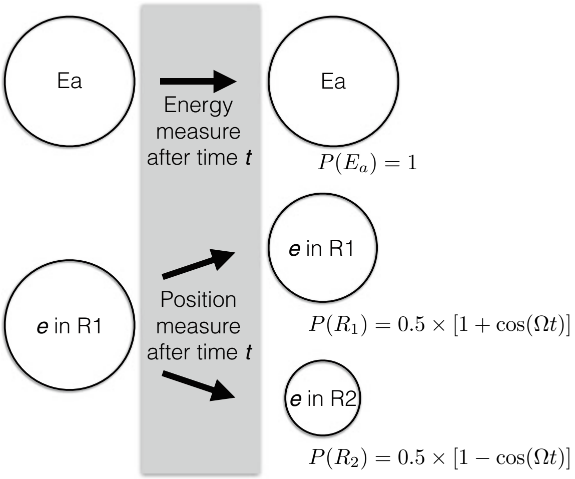

Ea
Energy measure after time *t*
Ea
$P(E_a) = 1$
e in R1
Position measure after time *t*
e in R1
$P(R_1) = 0.5 \times [1 + \cos(\Omega t)]$
e in R2
$P(R_2) = 0.5 \times [1 - \cos(\Omega t)]$

Fig. 1.3 Top: After measuring the energy, the probability of measuring the same energy again after a time t is always equal to 1. Bottom: After measuring the position at R_1, the probability of measuring the same position again after a time t changes over time

it is the difference between the two possible energies divided by the so-called **Planck constant** $\hbar$. The constant $\hbar$ was introduced by Planck to explain the blackbody spectrum, a topic we do not cover in this book, and it has the dimensions of energy times time or, equivalently, momentum times position:

$$\hbar = 1.055 \times 10^{-34} \mathrm{J \cdot s}. \tag{1.5}$$

As we see, all the equations of quantum mechanics contain this constant. We also observe that the electron can only be found in either R_1 or R_2, and thus the sum of the probabilities $P(R_1) + P(R_2) = 1$. From Eq. (1.3), we can then deduce:

$$P(R_2) = 0.5 \times [1 - \cos(\Omega t)]. \tag{1.6}$$

In Fig. 1.3, we graphically summarize this experimental evidence.

1.2 Quantum Solution—The First Five Postulates

The solution to the experimental puzzle took years, and we present it in this section. As we see, it is necessary to abandon some familiar concepts to understand what happens when systems are on the nanoscale. Although the quantum view and the quantum rules may seem absurd, we anticipate that they have never been contradicted by experiments.

Let's begin with a completely general consideration. Physics is a science that uses mathematical laws primarily for two purposes:

(1) To relate the properties of a given system (for example, in the ideal gas law, pressure, volume, and temperature of the "ideal gas" system are related).

(2) To predict how the properties of a given system change over time using time-differential equations (for example, Newton's law for the "particle" system or Maxwell's equations for the "electromagnetic field" system).

For physics to be a quantitative science, all properties must be measurable. In fact, a law of physics is valid if and only if it is experimentally verified. Let's go back to the electron in the H_2^+ ion discussed in the previous section. We have learned that if we measure the position, the result of an energy measurement is not unique. And if we measure the energy, the result of a position measurement is not unique either. This means that we have no hope of writing equations in terms of position and momentum, such as Newton's equation $\frac{dp}{dt} = F(r)$, as these equations would predict a specific value of r and p, and therefore r and E, at every instant of time. The first two postulates of quantum mechanics arise from the following observation. Consider a measurable property, which we call **observable**, and take note of the possible values of the measurement result. In the case of the H_2^+ ion, the measurement of the observable position provided only two values, R_1 and R_2. Since it is not possible to know anything else with absolute certainty (remember that a subsequent energy measurement did not always yield the same value), we must conclude that *the electron in a* H_2^+ *ion is entirely characterized by the position value alone*. We then assign a ket $|R_1\rangle$ to the electron when R_1 is measured, and a ket $|R_2\rangle$ when R_2 is measured. These kets describe the state of the system. We assume that these kets form the *orthonormal basis of a Hilbert space* $\mathcal{H}$, thus the scalar product

$$\langle R_i|R_j\rangle = \delta_{ij}, \quad i, j = 1, 2. \tag{1.7}$$

If instead of the position, we had chosen to measure the energy, we could have followed the same reasoning. Since it is not possible to know anything else with absolute certainty (remember that a subsequent measurement of the position did not always provide the same value, see Fig. 1.2), then the electron in a H_2^+ ion is entirely characterized by the value of the energy. Let's assign the ket $|E_a\rangle$ to the electron when the energy is measured to be E_a and the ket $|E_b\rangle$ when the energy is measured to be E_b. These kets form an orthonormal basis *of the same Hilbert space* $\mathcal{H}$ (the observable has changed, but the system is the same):

$$\langle E_i|E_j\rangle = \delta_{ij}, \quad i, j = a, b \tag{1.8}$$

As both $|R_1\rangle$, $|R_2\rangle$ and $|E_a\rangle$, $|E_b\rangle$ form a basis of $\mathcal{H}$, we can express one set in terms of the other as a linear combination:

$$|R_i\rangle = \sum_{j=a,b} \langle E_j|R_i\rangle|E_j\rangle, \qquad |E_i\rangle = \sum_{j=1,2} \langle R_j|E_i\rangle|R_j\rangle. \tag{1.9}$$

More generally, if we had chosen to measure a generic observable with possible values O_α and O_β, we would have assigned the ket $|O_\alpha\rangle$ to the electron in the first case and $|O_\beta\rangle$ in the second case. Furthermore, $|O_\alpha\rangle, |O_\beta\rangle$ would have formed an orthonormal basis of the same Hilbert space $\mathcal{H}$. This way of describing the electron is at the core of the

FIRST POSTULATE:

A system (the electron in a H_2^+ *in our example) is described by a ket* $|\Psi\rangle$ *that belongs to a Hilbert space* $\mathcal{H}$.

To determine the ket $|\Psi\rangle \in \mathcal{H}$, a measurement is necessary. Let's suppose we want to measure a certain observable (like position or energy in our example of the ion H_2^+), and we indicate the possible values of the measurement as $\{O_j\}$. In our example, $\{O_j\} = (R_1, R_2)$ if the observable is the position, and $\{O_j\} = (E_a, E_b)$ if the observable is the energy. The second postulate states that

SECOND POSTULATE:

The system immediately after measuring O_j *is described by the ket* $|O_j\rangle$, *regardless of the system's state before the measurement.*

Henceforth we interchangably say that "a system is described by a ket $|\Psi\rangle$" or that "the state of the system is the ket $|\Psi\rangle$". The second postulate is also known as the **collapse postulate**, as if the system is in a general ket $|\Psi\rangle$ just before the measurement, it collapses into $|O_j\rangle$ immediately after the measurement.

The third postulate of quantum mechanics concerns observables:

THIRD POSTULATE:

For every observable that can yield values O_j *upon measurement, the following Hermitian operator is associated:*

$$\hat{O} = \sum_j O_j |O_j\rangle\langle O_j|, \tag{1.10}$$

where the $\{|O_j\rangle\}$ *form an orthonormal basis of* $\mathcal{H}$.

From now on, we put a hat, represented by the symbol "ˆ", above a letter to denote an operator. Therefore, if O is an observable, then $\hat{O}$ is the associated operator, O_j are the eigenvalues of $\hat{O}$, and $|O_j\rangle$ are the eigenvectors (or better eigenkets) of $\hat{O}$ with eigenvalue O_j. In our example of the electron in the H_2^+ ion, the position observable and the energy observable are associated with the operators:

$$\hat{R} = \sum_{j=1,2} R_j |R_j\rangle\langle R_j|, \qquad \hat{E} = \sum_{j=a,b} E_j |E_j\rangle\langle E_j|. \tag{1.11}$$

The first three postulates essentially lay down the mathematical apparatus, and by themselves, they do not allow us to compute anything. For this, it is necessary to introduce two additional postulates. Thanks to the fourth postulate, we can *calculate* the probability of measuring a certain value for a given observable. The fourth postulate states that

FOURTH POSTULATE:

If the system is described by the ket $|\Psi\rangle \in \mathcal{H}$ *with normalization* $\langle\Psi|\Psi\rangle = 1$, *then the probability* $P(O_j)$ *of measuring the value* O_j *for the observable* $\hat{O}$ *is given by*

$$P(O_j) = |\langle O_j|\Psi\rangle|^2. \tag{1.12}$$

With the fourth postulate, we can begin to test the mathematical apparatus that we are setting up. Let's consider Fig. 1.2. According to the second postulate, right after measuring R_1, the state of the system is $|\Psi\rangle = |R_1\rangle$. From the fourth postulate, the probability of measuring energy E_j is then:

$$P(E_j) = |\langle E_j|R_1\rangle|^2 \simeq 0.5 = \frac{1}{2}. \tag{1.13}$$

In the last identity, we used the experimental data provided by Eq. (1.2). From Eq. (1.13), it follows that $\langle E_j|R_1\rangle = e^{\mathrm{i}\theta_j}/\sqrt{2}$, where θ_j are phases that we cannot determine at the moment. Taking this result into account in the first of Eq. (1.9), we find:

$$|R_1\rangle = \frac{e^{\mathrm{i}\theta_a}}{\sqrt{2}}|E_a\rangle + \frac{e^{\mathrm{i}\theta_b}}{\sqrt{2}}|E_b\rangle. \tag{1.14}$$

The Eq. (1.14) allows us to express the ket $|R_2\rangle$ as a linear combination of $|E_a\rangle$ and $|E_b\rangle$ since we know that $\langle R_2|R_2\rangle = 1$ and $\langle R_1|R_2\rangle = 0$ (see third postulate). Using the first of Eq. (1.9), from $\langle R_2|R_2\rangle = 1$, we find:

$$|\langle E_a|R_2\rangle|^2 + |\langle E_b|R_2\rangle|^2 = 1, \tag{1.15}$$

and from $\langle R_1|R_2\rangle = 0$, we find:

$$\frac{e^{-\mathrm{i}\theta_a}}{\sqrt{2}}\langle E_a|R_2\rangle + \frac{e^{-\mathrm{i}\theta_b}}{\sqrt{2}}\langle E_b|R_2\rangle = 0. \tag{1.16}$$

From these last two equations, it is straightforward to derive $\langle E_a|R_2\rangle = e^{\mathrm{i}\theta_a}/\sqrt{2}$ and $\langle E_b|R_2\rangle = -e^{\mathrm{i}\theta_b}/\sqrt{2}$. The reader can independently check that by substituing these results into (1.15) and (1.16) we obtain an identity. Thus,

$$|R_2\rangle = \frac{e^{\mathrm{i}\theta_a}}{\sqrt{2}}|E_a\rangle - \frac{e^{\mathrm{i}\theta_b}}{\sqrt{2}}|E_b\rangle. \tag{1.17}$$

Well, now we are ready to make some predictions. Let's assume we have measured energy E_a and, therefore, the system is described by the ket $|E_a\rangle$. According to the fourth postulate, the probability of measuring the position R_i is:

$$P(R_i) = |\langle R_i|E_a\rangle|^2 = 1/2, \tag{1.18}$$

In the last step, we use Eqs. (1.14) and (1.17). The result we just obtain is in excellent agreement with the experiment, see Fig. 1.2. Therefore, from knowing the probabilities of measuring energy after measuring the position, we deduced the probabilities of measuring the positions after measuring the energy, and obtained the experimentally correct result. We can also deduce another result. If we measure the position and find R_1, then right after the measurement, $|\Psi\rangle = |R_1\rangle$ (second postulate). According to the fourth postulate, the probability of measuring R_1 immediately after is:

$$P(R_1) = |\langle R_1|R_1\rangle|^2 = 1 \tag{1.19}$$

while the probability of measuring R_2 is $P(R_2) = |\langle R_2|R_1\rangle|^2 = 0$. This is precisely what is found experimentally. In fact, the experimental probabilities of measuring R_1 and R_2 after a time t are given by Eqs. (1.3) and (1.6). So, to know the experimental probabilities right after the measurement, we need to evaluate Eqs. (1.3) and (1.6) at time $t = 0$. The experimental result is precisely what the theory predicts.

The fifth postulate is undoubtedly the most important as it represents the analogue of Newton's equation in classical mechanics. It allows us to calculate the temporal evolution of the system's state. Let's denote by $|\Psi(t)\rangle \in \mathcal{H}$ the ket that describes the system at time t. The fifth postulate, also known as the **Schrödinger equation**, states that:

FIFTH POSTULATE:

$|\Psi(t)\rangle$ satisfies the following first-order differential equation in time:

$$\mathrm{i}\hbar\frac{d}{dt}|\Psi(t)\rangle = \hat{E}|\Psi(t)\rangle, \tag{1.20}$$

where $\hat{E}$ is the energy operator.

In the case of the electron in the H_2^+ ion, the energy operator is given by the second equation in Eq. (1.11). In reality, the fifth postulate is slightly more general, but for now, we don't need its full generality. We will come back to it later.

The Schrödinger equation allows us to calculate the probability of the outcome of a measurement at time t and, therefore, verify the correctness of the theory by comparing it with the experiments shown in Fig. 1.3. Let's start by finding the most general solution of the Schrödinger equation in the case of the electron in the H_2^+ ion. We expand the generic ket $|\Psi(t)\rangle$ in the basis of eigenkets of $\hat{E}$:

$$|\Psi(t)\rangle = \sum_{j=a,b} c_j(t)|E_j\rangle. \tag{1.21}$$

The coefficients $c_j(t) = \langle E_j|\Psi(t)\rangle$ depend on time because $|\Psi(t)\rangle$ is a function of time. The Schrödinger equation provides:

$$\begin{aligned} \mathrm{i}\hbar\frac{d}{dt}|\Psi(t)\rangle &= \mathrm{i}\hbar\sum_{j=a,b}\frac{dc_j(t)}{dt}|E_j\rangle, \\ \hat{E}|\Psi(t)\rangle &= \sum_{j=a,b} c_j(t)\hat{E}|E_j\rangle = \sum_{j=a,b} E_j c_j(t)|E_j\rangle. \end{aligned} \tag{1.22}$$

In the last identity, we use that $\hat{E}|E_j\rangle = E_j|E_j\rangle$. By equating the right-hand sides, we find:

$$\sum_{j=a,b}\left(\mathrm{i}\hbar\frac{dc_j(t)}{dt} - E_j c_j(t)\right)|E_j\rangle = 0. \tag{1.23}$$

This equation is satisfied if and only if, for each j, the term in parentheses is zero, as the kets $|E_j\rangle$ are mutually orthonormal and, therefore, independent. We therefore need to find the solution of the differential equation:

$$\mathrm{i}\hbar\frac{dc_j(t)}{dt} - E_j c_j(t) = 0. \tag{1.24}$$

This is a first-order differential equation with constant coefficients and is homogeneous. It is easy to verify that the solution is:

$$c_j(t) = e^{-\mathrm{i}E_j t/\hbar}c_j(0). \tag{1.25}$$

Evaluating this equation at $t = 0$, we correctly find $c_j(0) = c_j(0)$. Alright, now let's turn to the experiments in Fig. 1.3.

In the first experiment, we perform a measurement of energy and find the value E_a. Therefore, according to the second postulate, immediately after the measurement, the system is described by the ket $|E_a\rangle$. Let's choose the time of measurement as the initial instant, that is, $t = 0$, and write $|\Psi(0)\rangle = |E_a\rangle$. From Eq. (1.21) evaluated at $t = 0$, we obtain the initial conditions for the coefficients: $c_a(0) = 1$ and $c_b(0) = 0$. Therefore, the ket at time t is:

$$|\Psi(t)\rangle = e^{-\mathrm{i}E_a t/\hbar}|E_a\rangle. \tag{1.26}$$

According to the fourth postulate, the probability of measuring E_a at time t is:

$$P(E_a) = |\langle E_a|\Psi(t)\rangle|^2 = 1, \tag{1.27}$$

which is in agreement with the experiment, see Fig. 1.3.

Let's now move to the second experiment. In this case, at time $t = 0$, a measurement of position is performed, and the result is R_1. Therefore, based on the second postulate, the state at time $t = 0$ is $|\Psi(0)\rangle = |R_1\rangle$. Using Eq. (1.14), it follows that:

$$|\Psi(0)\rangle = c_a(0)|E_a\rangle + c_b(0)|E_b\rangle = |R_1\rangle = \frac{e^{\mathrm{i}\theta_a}}{\sqrt{2}}|E_a\rangle + \frac{e^{\mathrm{i}\theta_b}}{\sqrt{2}}|E_b\rangle. \tag{1.28}$$

From this, we obtain the initial conditions for the coefficients:

$$c_a(0) = \frac{e^{\mathrm{i}\theta_a}}{\sqrt{2}}, \qquad c_b(0) = \frac{e^{\mathrm{i}\theta_b}}{\sqrt{2}}. \tag{1.29}$$

Therefore, in the second experiment, the ket at time t is given by:

$$|\Psi(t)\rangle = \frac{e^{\mathrm{i}\theta_a - \mathrm{i}E_a t/\hbar}}{\sqrt{2}}|E_a\rangle + \frac{e^{\mathrm{i}\theta_b - \mathrm{i}E_b t/\hbar}}{\sqrt{2}}|E_b\rangle. \tag{1.30}$$

According to the fourth postulate, the probability of measuring R_1 at time t is:

$$P(R_1) = |\langle R_1|\Psi(t)\rangle|^2 = \left|\frac{e^{\mathrm{i}\theta_a - \mathrm{i}E_a t/\hbar}}{\sqrt{2}}\langle R_1|E_a\rangle + \frac{e^{\mathrm{i}\theta_b - \mathrm{i}E_b t/\hbar}}{\sqrt{2}}\langle R_1|E_b\rangle\right|^2. \tag{1.31}$$

From Eq. (1.14), we have:

$$\langle R_1|E_j\rangle = \langle E_j|R_1\rangle^* = \frac{e^{-\mathrm{i}\theta_j}}{\sqrt{2}}, \qquad j = a, b \tag{1.32}$$

and therefore:

$$P(R_1) = \frac{1}{4}\left|e^{-\mathrm{i}E_a t/\hbar} + e^{-\mathrm{i}E_b t/\hbar}\right|^2 = \frac{1}{2}\left[1 + \cos(\Omega t)\right] \tag{1.33}$$

which is in perfect agreement with the experimental data in Eq. (1.3).

1.3 Expectation Value, Variance, and General Considerations

In the previous section, we have laid the foundations of quantum mechanics. In addition to the mathematical framework that we will explore further, we have introduced a completely new description of the world around us. To begin with, if we measure a certain observable on a large number of systems, all prepared in the same way, the result is not always the same! We can't help it; that's how the world works at the nanoscale. The best we can predict is not the value of the measurement but the probability of obtaining that measurement.

The results of measuring a given observable are the eigenvalues O_j of the operator $\hat{O}$ associated with that observable. The probability of measuring a certain O_j is given by $P(O_j) = |\langle O_j|\Psi\rangle|^2$, where $|\Psi\rangle$ is the ket that describes the state of the system at the instant the measurement is performed, and $|O_j\rangle$ is the eigenket of $\hat{O}$ with eigenvalue O_j.

From the knowledge of probabilities, we can calculate the **average value**, also known as the **expectation value**, of an observable:

$$\langle\hat{O}\rangle = \sum_j P(O_j)O_j = \sum_j \langle\Psi|O_j\rangle O_j\langle O_j|\Psi\rangle = \langle\Psi|\hat{O}|\Psi\rangle, \tag{1.34}$$

where, in the last step, we use Eq. (1.10) from the third postulate, which states that $\sum_j O_j|O_j\rangle\langle O_j| = \hat{O}$. We can also get an idea of the probability distribution by calculating the **variance**, or **standard deviation**, defined as the square root of:

$$\sigma_O^2 = \sum_j P(O_j)O_j^2 - \langle\hat{O}\rangle^2 = \sum_j P(O_j)(O_j - \langle\hat{O}\rangle)^2 = \langle\left(\hat{O} - \langle\hat{O}\rangle\right)^2\rangle. \tag{1.35}$$

The smaller σ_O^2 is, the larger the probabilities $P(O_j)$ are when $O_j \sim \langle\hat{O}\rangle$, and they are small otherwise. In these cases, the measurement of the observable always gives a result very close to $\langle\hat{O}\rangle$. At macroscopic scales, the variances are very small, and the average values of observables, such as position and momentum, satisfy the equations of Newton. Therefore, classical mechanics follows from quantum mechanics by identifying classical quantities with quantum average values.

However, there are still several open questions to investigate before showing the transition from quantum mechanics to classical mechanics. For example: Why does the minimum of measurable energy in the H_2^+ ion not coincide with that of classical physics? How do we write the observables position and energy in systems other than the H_2^+ ion? To proceed, it is necessary to introduce one final postulate. Before doing so, however, we must discuss the concept of probability density and then the Lagrangian and Hamiltonian formalism of classical physics.

1.4 Observables with Continuum Spectrum and Wavefunction

In nature, there exist many "one-dimensional" systems. These are systems that extend along one direction over nearly microscopic distances (of the order of 10^{-6}–10^{-7} m), while they are confined along the other two directions, extending over nanoscopic distances (of the order of 10^{-8}–10^{-9} m). Examples of such systems include carbon nanotubes, polymer chains, the so-called quantum wires, and more. Let's consider

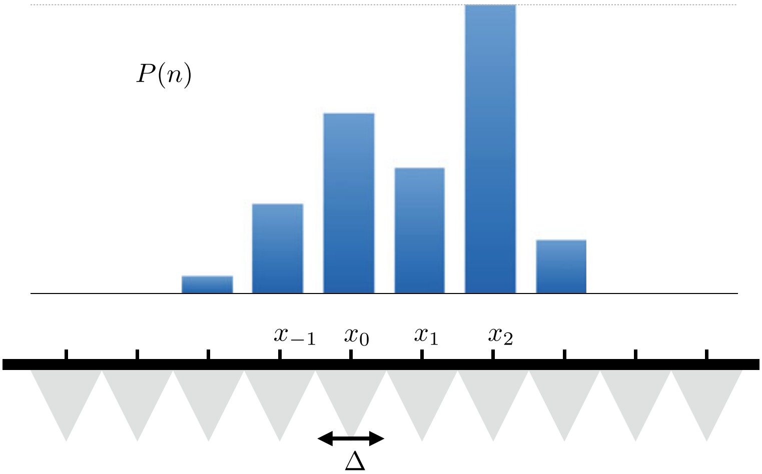


Fig. 1.4 Probability histogram of measuring the electron in a vicinity of x_n

having one of these one-dimensional systems available, and we choose the coordinate system so that the x-axis aligns with the longest direction, the microscopic one. Suppose we are interested in measuring the position of an electron within this system, and we set up detectors along the system. Detectors are devices that emit a "click" when an electron is in their vicinity. Let Δ represent the extent of the detectors, and let's arrange them next to each other at positions $x_j = j\Delta$, as illustrated in Fig. 1.4. Now, imagine preparing our electron in a certain state described by the ket $|\Psi\rangle$ and immediately hearing a click. If the click comes from the n-th detector, then right after the measurement, we know that the electron is within a vicinity of Δ around x_n, and the state ket $|\Psi\rangle$ collapses (according to the postulate) onto the ket that describes the electron within this vicinity of x_n. Let's denote this ket as $|n\rangle$. By repeating the experiment a large number $K \gg 1$ of times (each time preparing the electron in the same state $|\Psi\rangle$) and noting, for each detector, the number k_n of times the click comes from the nth detector, we can construct the probability

$$P(n) = \frac{k_n}{K} \tag{1.36}$$

of measuring the electron within a vicinity of x_n. An example of these probabilities is depicted in Fig. 1.4 as a histogram. According to the fourth postulate, this probability is identical to

$$P(n) = |\langle n|\Psi\rangle|^2 \,. \tag{1.37}$$

Immediately after the click of, let's say, the detector at x_n, the electron is located within a vicinity of x_n, and thus the probability of finding it within a vicinity of $x_{n'}$ with $n' \neq n$ is zero. According to the collapse postulate, right after the click, the electron is described by $|n\rangle$, and therefore the probability of finding it at $x_{n'}$ is given by $P(n') = \left|\langle n'|n\rangle\right|^2$. Since this probability must be zero for $n' \neq n$ and unity for $n' = n$, we conclude that

$$\langle n'|n\rangle = \delta_{nn'}. \tag{1.38}$$

The experiment just conducted justifies the final part of the third postulate. In fact, the third postulate tells us that the position operator is given by

$$\hat{x} = \sum_n (n\Delta)|n\rangle\langle n| \tag{1.39}$$

and that the kets $|n\rangle$ form an orthonormal basis for the Hilbert space $\mathcal{H}$ of our electron. As we have just seen from Eq. (1.38), the fact that the kets $|n\rangle$ are orthonormal expresses a natural physical conclusion arising from the collapse and the fourth postulate. The fact that they form a basis can be justified experimentally in the following manner. Suppose, for the sake of contradiction, that they are not a basis. Hence, there must exist a ket $|\chi\rangle$ orthogonal to all the $|n\rangle$. If we were to prepare the initial state of the electron in $|\Psi\rangle = |\chi\rangle$, then the probability that the n-th detector clicks would be $|\langle n|\chi\rangle|^2 = 0$ for all n. But this would imply that the electron is nowhere, which is absurd.

Having established that the $|n\rangle$ are an orthonormal basis, we can expand a general state ket $|\Psi\rangle$ in this basis. For any general orthonormal basis, the completeness relation holds, also known as the **resolution of the identity**,

$$\boxed{\sum_n |n\rangle\langle n| = \hat{\mathbb{1}}} \tag{1.40}$$

and therefore

$$|\Psi\rangle = \sum_n |n\rangle\langle n|\Psi\rangle = \sum_n \Psi_n|n\rangle, \qquad \text{with} \quad \Psi_n = \langle n|\Psi\rangle. \tag{1.41}$$

As seen from Eq. (1.37), the probability of finding the electron within a vicinity of x_n is simply the square modulus of $\langle n|\Psi\rangle$: $P(n) = |\langle n|\Psi\rangle|^2$. It's important to note that these probabilities sum up to one, i.e., $\sum_n P(n) = 1$, only if the ket $|\Psi\rangle$ is normalized to one, i.e., $\langle\Psi|\Psi\rangle = 1$. In fact,

$$\sum_n P(n) = \sum_n |\Psi_n|^2 = \sum_n \Psi_n^*\Psi_n = \sum_n \langle\Psi|n\rangle\langle n|\Psi\rangle = \langle\Psi|\underbrace{\left(\sum_n |n\rangle\langle n|\right)}_{1}|\Psi\rangle =$$
$$= \langle\Psi|\Psi\rangle \tag{1.42}$$

So, if the ket $|\Psi\rangle$ is not normalized to unity, the sum of the probabilities does not add up to unity. From an interpretational standpoint, nothing changes, of course, in the sense that the ket $|\Psi\rangle$ and the ket $C|\Psi\rangle$, *with C being an arbitrary complex number*, describe the same physical state. However, the sum of probabilities in the second case is $|C|^2$ times larger. To obtain probabilities normalized to unity, it is sufficient to divide by $|C|^2$. It is also noteworthy that if $C = e^{i\theta}$ with θ being real, then both $|\Psi\rangle$ and $C|\Psi\rangle = e^{i\theta}|\Psi\rangle$ are normalized to unity. Therefore, normalization alone is not enough to uniquely determine the state ket. However, this arbitrariness doesn't affect the physical results in any way, as the phase factor always cancels out. In other words, we are free to choose the phase θ we want, as long as once the choice is made, we consistently use in all derivation the chosen phase.

Let's now suppose that we are able to construct increasingly precise detectors, thereby reducing the space Δ they occupy. Ideally, we are interested in the limiting case of practically point-like detectors, which corresponds to the limit $\Delta \to 0$. As Δ approaches zero, the probability of measuring an electron within a vicinity Δ of x_n tends to zero. It's much more useful in this case to talk about the probability of finding the electron within a certain spatial interval. Therefore, we introduce the concept of **probability density** defined as,

$$\boxed{P(x_n) = \lim_{\Delta\to 0} \frac{P(n)}{\Delta} = \lim_{\Delta\to 0} \frac{|\Psi_n|^2}{\Delta}} \tag{1.43}$$

From this definition, it follows that if we wanted to know the probability of finding the electron between two points x_a and x_b, we would need to calculate the integral $\int_{x_a}^{x_b} dx\, P(x)$. Equation (1.43) also suggests defining what is known as the **wavefunction**,

$$\boxed{\Psi(x_n) = \lim_{\Delta\to 0} \frac{\Psi_n}{\sqrt{\Delta}}} \tag{1.44}$$

so that we can rewrite the probability density directly as

$$\boxed{P(x) = |\Psi(x)|^2} \tag{1.45}$$

In the limit $\Delta \to 0$, it is also convenient to define *unnormalized* kets. Nothing too complex, so don't be alarmed. Let's consider the expansion of the ket $|\Psi\rangle$ in Eq. (1.41). It can be rewritten as,

$$|\Psi\rangle = \sum_n \Delta \frac{\Psi_n}{\sqrt{\Delta}} \frac{|n\rangle}{\sqrt{\Delta}}\,, \tag{1.46}$$

where we have simply multiplied and divided by Δ. If we define the kets (remember that $x_n = n\Delta$)

$$\boxed{|x_n\rangle = \lim_{\Delta\to 0} \frac{|n\rangle}{\sqrt{\Delta}}} \tag{1.47}$$

then in the limit $\Delta \to 0$, the expansion in Eq. (1.46) yields

$$|\Psi\rangle = \lim_{\Delta\to 0} \sum_n \Delta\ \Psi(x_n)|x_n\rangle = \int dx\ \Psi(x)|x\rangle, \tag{1.48}$$

where in the last step we used the definition of an integral. Note that the wave function can also be written as the inner product between $|x_n\rangle$ and $|\Psi\rangle$, as per Eq. (1.44),

$$\Psi(x_n) = \lim_{\Delta\to 0} \frac{\langle n|\Psi\rangle}{\sqrt{\Delta}} = \langle x_n|\Psi\rangle. \tag{1.49}$$

The reason the kets $|x_n\rangle$ are not normalized becomes evident. We find that

$$\langle x_{n'}|x_n\rangle = \lim_{\Delta\to 0} \frac{\langle n'|n\rangle}{\Delta} = \lim_{\Delta\to 0} \frac{\delta_{nn'}}{\Delta}, \tag{1.50}$$

thus the normalization tends to infinity for $n = n'$. This fact is not problematic for two reasons. Firstly, as we have already pointed out, the physical state of a system is independent of the normalization of the ket, and therefore it remains well-defined. In our case, the ket $|x\rangle$ describes an electron *exactly* at x (rather than in its vicinity as the kets $|n\rangle$ did). Secondly, in all mathematical expressions, the divergence caused by the $1/\Delta$ factor is compensated by infinitesimals of order Δ, as can be seen, for example, in Eq. (1.46), and ultimately, the results of calculations are always finite.

Equation (1.50) can be rewritten in a more familiar form. Let's consider the integral of a function $f(x)$ multiplied by the Dirac delta function[1] $\delta(x - x')$:

$$\int dx f(x)\delta(x - x') = f(x'). \tag{1.51}$$

Dividing the x-axis into intervals of length Δ and defining as before $x_n = n\Delta$ and $x_{n'} = n'\Delta$, we can approximate Eq. (1.51) as

$$\sum_n \Delta f(x_n)\delta(x_n - x_{n'}) \simeq f(x_{n'}), \tag{1.52}$$

where the symbol $\simeq$ becomes an equality in the limit $\Delta \to 0$. The equation above implies that $\Delta\delta(x_n - x_{n'}) \simeq \delta_{nn'}$ or equivalently $\delta(x_n - x_{n'}) \simeq \delta_{nn'}/\Delta$. Taking the limit $\Delta \to 0$, we then conclude that

$$\delta(x_n - x_{n'}) = \lim_{\Delta\to 0} \frac{\delta_{nn'}}{\Delta}. \tag{1.53}$$

---

[1] For the definition and properties of the Dirac delta function, please refer to Appendix A.

Therefore, Eq. (1.50) tells us that the inner product between two unnormalized kets $|x\rangle$ and $|x'\rangle$ is equal to the Dirac delta function $\delta(x - x')$:

$$\boxed{\langle x'|x\rangle = \delta(x - x')} \tag{1.54}$$

There are two more important relations to derive in the limit $\Delta \to 0$. The first one concerns the position operator in Eq. (1.39). Multiplying and dividing by Δ, taking into account that $x_n = n\Delta$, and using the definition in Eq. (1.47), we find in the limit $\Delta \to 0$:

$$\hat{x} = \lim_{\Delta\to 0} \sum_n \Delta\ x_n \frac{|n\rangle}{\sqrt{\Delta}} \frac{\langle n|}{\sqrt{\Delta}} = \lim_{\Delta\to 0} \sum_n \Delta\ x_n |x_n\rangle\langle x_n| = \int dx\ x|x\rangle\langle x|. \tag{1.55}$$

The second one concerns the resolution of the identity in Eq. (1.40). Again, multiplying and dividing by Δ, we find in the limit $\Delta \to 0$:

$$\lim_{\Delta\to 0} \sum_n \Delta\ \frac{|n\rangle}{\sqrt{\Delta}} \frac{\langle n|}{\sqrt{\Delta}} = \lim_{\Delta\to 0} \sum_n \Delta\ |x_n\rangle\langle x_n| = \int dx\ |x\rangle\langle x| = \hat{\mathbb{1}}. \tag{1.56}$$

We can easily verify the correctness of this latter identity as follows:

$$\boxed{|\Psi\rangle = \hat{\mathbb{1}}|\Psi\rangle = \int dx\ |x\rangle\langle x|\Psi\rangle = \int dx\ \Psi(x)|x\rangle} \tag{1.57}$$

and the last expression matches that of Eq. (1.48).

The position operator in Eq. (1.55) is an operator with **continuum spectrum**, meaning that its eigenvalues are all possible values of x (a set isomorphic to the set of real numbers and therefore continuous). We will encounter other continuous spectrum operators such as momentum or energy. These operators have the form:

$$\hat{O} = \int dO\ O|O\rangle\langle O| \tag{1.58}$$

and the kets $|O\rangle$ have a scalar product:

$$\langle O'|O\rangle = \delta(O - O'). \tag{1.59}$$

It's straightforward to verify that the ket $|O\rangle$ is an eigenket of $\hat{O}$ with eigenvalue O:

$$\hat{O}|O\rangle = \int dO'\ O'|O'\rangle\langle O'|O\rangle = \int dO'\ O'|O'\rangle\delta(O' - O) = O|O\rangle, \tag{1.60}$$

and the resolution of the identity becomes:

$$\int dO|O\rangle\langle O| = 1. \tag{1.61}$$

1.5 Langrangian and Hamiltonian Formalism

To formulate the last postulate, we need to introduce the Lagrangian formalism first, followed by the Hamiltonian formalism

1.5.1 Lagrangian Formalism—Euler-Lagrange Equations

The Lagrangian formalism is particularly useful for solving classical mechanics problems where particles are subject to both external forces and constraint forces that limit their motion. Consider, for instance, a ball constrained to move inside a rigid tube shaped like a semicircle with radius R, as illustrated in Fig. 1.5 (left). This ball will experience both gravitational forces and constraint forces that confine its motion along the tube. In the presence of constraints, it's convenient to express the particle's coordinate $\mathbf{r}$ in terms of the *degrees of freedom* that we find most suitable. Let's consider the example of Fig. 1.5 (left) again and choose a reference frame with the origin at the center of the circle, the z-axis orthogonal to the circle, and the x-axis passing through the endpoints of the semicircle along which the particle moves. The particle's coordinates must then satisfy the constraints,

$$z = 0, \qquad y = \sqrt{R^2 - x^2}. \tag{1.62}$$

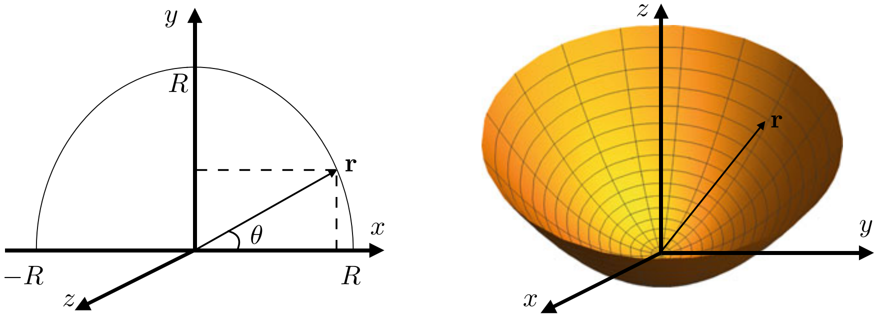


Fig. 1.5 Examples of constrained motion. Left: a particle is constrained to move along a semicircle. Right: a particle is constrained to move on the surface of a paraboloid

So, the only degree of freedom is $x \in (-R, R)$, and the entire coordinate $\mathbf{r} = (x, y, z)$ can be expressed in terms of x: $\mathbf{r} = \mathbf{r}(x) = (x, \sqrt{R^2 - x^2}, 0)$. Alternatively, we could have expressed the constraint in terms of the angle θ that the vector $\mathbf{r}$ forms with the x-axis:

$$z = 0, \qquad x = R\cos\theta, \qquad y = R\sin\theta. \tag{1.63}$$

In this case, the only degree of freedom is $\theta \in (0, \pi)$, and the entire coordinate $\mathbf{r} = (x, y, z)$ can be expressed in terms of θ: $\mathbf{r} = \mathbf{r}(\theta) = (R\cos\theta, R\sin\theta, 0)$.

The number M of degrees of freedom depends on the constraints; a particle in 3 dimensions subject to $K \leq 3$ constraints has $M = 3 - K$ degrees of freedom. In our example, we have $K = 2$ constraints (one enforcing $z = 0$, and the other relating x and y), so the number of degrees of freedom is $M = 3 - 2 = 1$. An example of a particle subjected to a single constraint is illustrated in Fig. 1.5 (right). In this case, the particle is confined to move on the surface of a paraboloid, so the coordinates x and y can vary between $-\infty$ and ∞, and for a certain combination of x and y, the coordinate z is given by

$$z = x^2 + y^2. \tag{1.64}$$

We therefore have a single constraint ($K = 1$) and $M = 3 - K = 2$ degrees of freedom, namely x and y. The entire coordinate $\mathbf{r} = (x, y, z)$ can be expressed in terms of x and y in this case: $\mathbf{r} = \mathbf{r}(x, y) = (x, y, x^2 + y^2)$. Even in the case of the paraboloid, the choice of degrees of freedom is not unique. For instance, we could express the particle's coordinates as

$$x = \ell\cos\theta, \qquad y = \ell\sin\theta, \qquad z = \ell^2, \tag{1.65}$$

and let the angle θ vary in the interval $(0, 2\pi)$ and the length ℓ range from 0 to ∞. In this case, the degrees of freedom are θ and ℓ, and the entire coordinate $\mathbf{r} = (x, y, z)$ can be expressed in terms of them: $\mathbf{r} = \mathbf{r}(\theta, \ell) = (\ell\cos\theta, \ell\sin\theta, \ell^2)$.

We denote by $q = (q_1, \dots, q_M)$ the set of degrees of freedom that we choose to use. In the example of the tube, we could choose $q = (q_1) = (x)$ or $q = (q_1) = (\theta)$, while in the case of the paraboloid, we could choose $q = (q_1, q_2) = (x, y)$ or $q = (q_1, q_2) = (\theta, \ell)$. As we have seen, the coordinate $\mathbf{r}$ can be expressed in terms of the degrees of freedom q: $\mathbf{r} = \mathbf{r}(q)$. Denoting the mass of the particle as m, Newton's equations tell us that

$$m\frac{d^2\mathbf{r}}{dt^2} = \mathbf{F} + \mathbf{F}^{\text{constr}} \tag{1.66}$$

where $\mathbf{F}$ is the active force (gravitational, electromagnetic, etc.), while $\mathbf{F}^{\text{constr}}$ is the force due to constraints. Constraint forces are always orthogonal to the infinitesimal displacements $\delta\mathbf{r}$ that the particle can undergo, and therefore they are orthogonal to its velocity $\mathbf{v} = d\mathbf{r}/dt$. It follows that

$$\left(m\frac{d^2\mathbf{r}}{dt^2} - \mathbf{F}\right) \cdot \mathbf{v} = 0. \tag{1.67}$$

Alright, let's work with this expression now. Since $\mathbf{r} = \mathbf{r}(q)$, using the chain rule

$$\mathbf{v} = \frac{d\mathbf{r}}{dt} = \sum_\alpha \frac{\partial \mathbf{r}}{\partial q_\alpha}\frac{dq_\alpha}{dt} = \sum_\alpha \frac{\partial \mathbf{r}}{\partial q_\alpha}\dot{q}_\alpha, \tag{1.68}$$

where in the last step we introduce the notation to indicate the time derivative of a function with a dot above the function itself. We then have

$$m\frac{d^2\mathbf{r}}{dt^2} \cdot \mathbf{v} = \sum_\alpha m\frac{d^2\mathbf{r}}{dt^2} \cdot \frac{\partial \mathbf{r}}{\partial q_\alpha}\dot{q}_\alpha = \sum_\alpha \left[\frac{d}{dt}\left(m\frac{d\mathbf{r}}{dt} \cdot \frac{\partial \mathbf{r}}{\partial q_\alpha}\right) - m\frac{d\mathbf{r}}{dt} \cdot \frac{d}{dt}\frac{\partial \mathbf{r}}{\partial q_\alpha}\right]\dot{q}_\alpha. \tag{1.69}$$

From Eq. (1.68), we see that the change in velocity $\delta\mathbf{v}$ due to the change in velocity $\delta\dot{q}_\beta$ of only the degree of freedom β is $\delta\mathbf{v} = (\partial\mathbf{r}/\partial q_\beta)\delta\dot{q}_\beta$ or equivalently

$$\frac{\partial \mathbf{v}}{\partial \dot{q}_\beta} = \frac{\partial \mathbf{r}}{\partial q_\beta}. \tag{1.70}$$

We can use this relation in Eq. (1.69) to obtain

$$\begin{aligned} m\frac{d^2\mathbf{r}}{dt^2} \cdot \mathbf{v} &= \sum_\alpha \left[\frac{d}{dt}\left(m\mathbf{v} \cdot \frac{\partial \mathbf{v}}{\partial \dot{q}_\alpha}\right) - m\mathbf{v} \cdot \frac{\partial \mathbf{v}}{\partial q_\alpha}\right]\dot{q}_\alpha \\ &= \sum_\alpha \left[\frac{d}{dt}\frac{\partial}{\partial \dot{q}_\alpha}\left(\frac{m}{2}v^2\right) - \frac{\partial}{\partial q_\alpha}\left(\frac{m}{2}v^2\right)\right]\dot{q}_\alpha, \end{aligned} \tag{1.71}$$

where we have defined the square of the velocity vector as $v^2 = \mathbf{v} \cdot \mathbf{v}$.

Now let's move on to the active forces. In general, $\mathbf{F}$ depends not only explicitly on time t but also on both the particle's position and velocity: $\mathbf{F} = \mathbf{F}(\mathbf{r}, \mathbf{v}, t)$. Let (F^x, F^y, F^z) be the three components of the force acting on the particle, and let $\mathbf{r} = (x, y, z)$ and $\mathbf{v} = (v^x, v^y, v^z)$ be the components of its position and velocity. In what follows, we assume that forces can be written as

$$F^x = -\frac{\partial U}{\partial x} + \frac{d}{dt}\frac{\partial U}{\partial v^x}, \qquad F^y = -\frac{\partial U}{\partial y} + \frac{d}{dt}\frac{\partial U}{\partial v^y}, \qquad F^z = -\frac{\partial U}{\partial z} + \frac{d}{dt}\frac{\partial U}{\partial v^z} \tag{1.72}$$

where $U = U(\mathbf{r}, \mathbf{v}, t)$ is a function that can depend on time and the position and velocity of all the particles. As we see, the form of the forces we are considering includes not only gravitational and elastic forces but also the Lorentz force. Let's manipulate the second term of Eq. (1.67)

$$\begin{aligned}\mathbf{F}\cdot\mathbf{v} &= \sum_\alpha \mathbf{F}\cdot\frac{\partial\mathbf{r}}{\partial q_\alpha}\dot{q}_\alpha\\ &= \sum_\alpha\left\{-\frac{\partial U}{\partial x}\frac{\partial x}{\partial q_\alpha}-\frac{\partial U}{\partial y}\frac{\partial y}{\partial q_\alpha}-\frac{\partial U}{\partial z}\frac{\partial z}{\partial q_\alpha}\right.\\ &\quad\left.+\left(\frac{d}{dt}\frac{\partial U}{\partial v^x}\right)\frac{\partial v^x}{\partial\dot{q}_\alpha}+\left(\frac{d}{dt}\frac{\partial U}{\partial v^y}\right)\frac{\partial v^y}{\partial\dot{q}_\alpha}+\left(\frac{d}{dt}\frac{\partial U}{\partial v^z}\right)\frac{\partial v^z}{\partial\dot{q}_\alpha}\right\}\dot{q}_\alpha,\end{aligned}\tag{1.73}$$

where for the last three terms we have used Eq. (1.70). In order to proceed further, we need to further restrict the cases under consideration:

Case 1: The function U does not depend on velocities, i.e., $U = U(\mathbf{r}(q), t)$, and thus $\frac{\partial U}{\partial v^i} = 0$ for $i = x, y, z$ (conservative forces).

Case 2: The coordinates x, y, z are linear combinations of the degrees of freedom, i.e., $x = \sum_\alpha c^x_\alpha q_\alpha$, $y = \sum_\alpha c^y_\alpha q_\alpha$, and $z = \sum_\alpha c^z_\alpha q_\alpha$, where the coefficients c^i_α (with $i = x, y, z$) are independent of time. In this case, $v^i = \sum_\alpha c^i_\alpha \dot{q}_\alpha$ (with $i = x, y, z$), and therefore $\frac{\partial v^i}{\partial \dot{q}_\alpha} = c^i_\alpha$ is time-independent.

In both case 1 and case 2, the sum of the first three terms yields $-\frac{\partial U}{\partial q_\alpha}$, while the sum of the last three terms yields

$$\begin{aligned}\left(\frac{d}{dt}\frac{\partial U}{\partial v^x}\right)\frac{\partial v^x}{\partial\dot{q}_\alpha}+\left(\frac{d}{dt}\frac{\partial U}{\partial v^y}\right)\frac{\partial v^y}{\partial\dot{q}_\alpha}+\left(\frac{d}{dt}\frac{\partial U}{\partial v^z}\right)\frac{\partial v^z}{\partial\dot{q}_\alpha} &= \frac{d}{dt}\left(\frac{\partial U}{\partial v^x}\frac{\partial v^x}{\partial\dot{q}_\alpha}+\frac{\partial U}{\partial v^y}\frac{\partial v^y}{\partial\dot{q}_\alpha}+\frac{\partial U}{\partial v^z}\frac{\partial v^z}{\partial\dot{q}_\alpha}\right)\\ &= \frac{d}{dt}\frac{\partial U}{\partial\dot{q}_\alpha}.\end{aligned}\tag{1.74}$$

Therefore

$$\mathbf{F}\cdot\mathbf{v} = \sum_\alpha\left(-\frac{\partial U}{\partial q_\alpha}+\frac{d}{dt}\frac{\partial U}{\partial\dot{q}_\alpha}\right)\dot{q}_\alpha.\tag{1.75}$$

Subtracting Eq. (1.75) from Eq. (1.71) and taking into account Eq. (1.67), we arrive at the following important result:

$$\sum_\alpha\left[\frac{d}{dt}\frac{\partial(T-U)}{\partial\dot{q}_\alpha}-\frac{\partial(T-U)}{\partial q_\alpha}\right]\dot{q}_\alpha = 0,\tag{1.76}$$

where we have introduced the kinetic energy

$$T = \frac{1}{2}mv^2.\tag{1.77}$$

The quantity

$$\boxed{\mathcal{L} = T - U}\tag{1.78}$$

is called **Lagrangian** of the system. Since Eq. (1.76) must hold for all physical trajectories, and the degrees of freedom q are independent of each other, it follows that each term in the sum must be zero. This leads us to the **Euler-Lagrange equations**

$$\boxed{\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{q}_\alpha} = \frac{\partial \mathcal{L}}{\partial q_\alpha}} \tag{1.79}$$

The advantage of these equations is that they are equations for the degrees of freedom, so we don't need to worry about including additional equations to describe the constraints. Moreover, the Euler-Lagrange equations are relatively straightforward to derive once $\mathcal{L} = \mathcal{L}(q, \dot{q}, t)$ is known. To obtain the latter, it suffices to express T and U in terms of $\boldsymbol{r}$ and $\boldsymbol{v}$ and then express the latter in terms of q and $\dot{q}$ using Eq. (1.68).

1.5.2 Classical Particle in an Electromagnetic Field

In the absence of constraints, the Lagrangian formalism provides an alternative way to obtain Newton's equations. In the case of a single particle with mass m and charge Q in an electromagnetic field, the equations of Newton are

$$\boxed{m\frac{d\mathbf{v}}{dt} = Q(\mathbf{E} + \frac{1}{c}\mathbf{v} \times \mathbf{B})} \tag{1.80}$$

where the right hand side is the Lorentz force with electric field $\mathbf{E}(\mathbf{r}, t)$ and magnetic field $\mathbf{B}(\mathbf{r}, t)$. Since there are no constraints, we can choose the degrees of freedom $\{q\} = (x, y, z)$ to be precisely the coordinates of the particle, and thus $\{\dot{q}\} = (v^x, v^y, v^z)$ are the components of its velocity. We can then rewrite the Newton's equation in components as follows

$$m\frac{d}{dt}\dot{q}_\alpha = QE_\alpha + \frac{Q}{c}\sum_{\beta\gamma} \varepsilon_{\alpha\beta\gamma}\dot{q}_\beta B_\gamma \tag{1.81}$$

where in the last term we use the **Levi-Civita tensor** to obtain the component α of the vector product between $\mathbf{v}$ and $\mathbf{B}$, see Appendix B. The electric and magnetic fields can always be obtained from a scalar potential ϕ and a vector potential $\mathbf{A}$ in the following way

$$\mathbf{E} = -\nabla\phi - \frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}, \qquad \mathbf{B} = \nabla \times \mathbf{A}, \tag{1.82}$$

which, component wise, read

$$E_\alpha = -\frac{\partial \phi}{\partial q_\alpha} - \frac{1}{c}\frac{\partial A_\alpha}{\partial t}, \qquad B_\gamma = \sum_{\mu\nu} \epsilon_{\gamma\mu\nu}\frac{\partial A_\nu}{\partial q_\mu}. \tag{1.83}$$

Substituting these expressions into Eq. (1.81) and using the identity, see Appendix B,

$$\sum_\gamma \varepsilon_{\alpha\beta\gamma}\varepsilon_{\gamma\mu\nu} = \sum_\gamma \varepsilon_{\gamma\alpha\beta}\varepsilon_{\gamma\mu\nu} = \delta_{\alpha\mu}\delta_{\beta\nu} - \delta_{\alpha\nu}\delta_{\beta\mu} \tag{1.84}$$

we find

$$m\frac{d}{dt}\dot{q}_\alpha = Q\left(-\frac{\partial \phi}{\partial q_\alpha} - \frac{1}{c}\frac{\partial A_\alpha}{\partial t}\right) + \frac{Q}{c}\sum_\beta \dot{q}_\beta\left(\frac{\partial A_\beta}{\partial q_\alpha} - \frac{\partial A_\alpha}{\partial q_\beta}\right) \tag{1.85}$$

that it is another equivalent way of writing the Newton's equation.

We now want to prove that the Euler-Lagrange equations with

$$U = Q\phi - \frac{Q}{c}\mathbf{v}\cdot\mathbf{A} = Q\phi - \frac{Q}{c}\sum_\beta \dot{q}_\beta A_\beta \tag{1.86}$$

are exactly Eq. (1.85). Writing the kinetic energy in Eq. (1.77) as $T = \frac{m}{2}\sum_\alpha \dot{q}_\alpha^2$, the Lagrangian becomes

$$\boxed{\mathcal{L}(\{q\},\{\dot{q}\},t) = \frac{m}{2}\sum_\alpha \dot{q}_\alpha^2 - Q\phi + \frac{Q}{c}\sum_\beta \dot{q}_\beta A_\beta} \tag{1.87}$$

We have

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{q}_\alpha} = \frac{d}{dt}\left(m\dot{q}_\alpha + \frac{Q}{c}A_\alpha\right) = m\frac{d}{dt}\dot{q}_\alpha + \frac{Q}{c}\frac{\partial A_\alpha}{\partial t} + \frac{Q}{c}\sum_\beta \frac{\partial A_\alpha}{\partial q_\beta}\dot{q}_\beta, \tag{1.88}$$

$$\frac{\partial \mathcal{L}}{\partial q_\alpha} = -Q\frac{\partial \phi}{\partial q_\alpha} + \frac{Q}{c}\sum_\beta \dot{q}_\beta\frac{\partial A_\beta}{\partial q_\alpha}. \tag{1.89}$$

By equating these last two equations, we obtain exactly Eq. (1.85).

1.5.3 Hamiltonian Formalism—Legendre Transform—Hamilton's Equations

The Lagrangian formalism leads to M second-order differential equations in time for the M degrees of freedom $\{q\}$, which are precisely the Euler-Lagrange equations.

In contrast, the Hamiltonian formalism allows us to have only first-order differential equations in time. The price to pay, as we see, is that the number of equations doubles.

Before introducing the Hamiltonian formalism, let's take a brief digression into what is known as the **Legendre transform**. Consider a function $f(x, y)$ and write its variation due to a change in the independent variables x and y

$$df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy. \tag{1.90}$$

The functions $u = \frac{\partial f}{\partial x}$ and $v = \frac{\partial f}{\partial y}$ are also functions of x and y. By inverting $u = \frac{\partial f}{\partial x}$, we can express x in terms of u and y: $x = x(u, y)$. The Legendre transform involves constructing a function $g(u, y)$ based on the function f:

$$g(u, y) = ux(u, y) - f(x(u, y), y). \tag{1.91}$$

The function g is called the Legendre transform of the function f. What is special about g is that its variation due to changes in u and y can be expressed as follows:

$$dg = udx + xdu - df \tag{1.92}$$

and taking into account that $df = udx + vdy$ we find

$$dg = xdu - vdy. \tag{1.93}$$

Therefore $x(u, y)$ and $v(u, y)$ can be obtained from

$$x = \frac{\partial g}{\partial u}, \qquad v = -\frac{\partial g}{\partial y}. \tag{1.94}$$

Let's return to our Lagrangian. From a mathematical perspective, the function $\mathcal{L}(\{q\}, \{\dot{q}\}, t)$ can be seen as a function of the independent variables $\{q\}$, $\{\dot{q}\}$, and t. If these variables undergo an infinitesimal variation, the Lagrangian varies according to the chain rule:

$$d\mathcal{L} = \sum_{\alpha} \left(\frac{\partial \mathcal{L}}{\partial q_\alpha} dq_\alpha + \frac{\partial \mathcal{L}}{\partial \dot{q}_\alpha} d\dot{q}_\alpha \right) + \frac{\partial \mathcal{L}}{\partial t} dt. \tag{1.95}$$

We define the **conjugate momentum** to the variable q_α as

$$\boxed{p_\alpha = \frac{\partial \mathcal{L}}{\partial \dot{q}_\alpha}} \tag{1.96}$$

We thus have M conjugate momenta, each a function of $\{q\}$, $\{\dot{q}\}$, and t. Taking into account the Euler-Lagrange equations, we can rewrite Eq. (1.95) as

$$d\mathcal{L} = \sum_\alpha (\dot{p}_\alpha dq_\alpha + p_\alpha d\dot{q}_\alpha) + \frac{\partial \mathcal{L}}{\partial t} dt. \tag{1.97}$$

Now, we use the definition of the conjugate momenta to express the $\dot{q}_\alpha$ in terms of $\{q\}$, $\{p\}$, and t, and we construct the following Legendre transform of the Lagrangian, known as the **Hamiltonian**,

$$\boxed{H(\{q\}, \{p\}, t) = \sum_\alpha \dot{q}_\alpha p_\alpha - \mathcal{L}(\{q\}, \{\dot{q}\}, t)} \tag{1.98}$$

The variation of H due to an infinitesimal variation of $\{q\}$, $\{p\}$ and t is

$$dH = \sum_\alpha (\dot{q}_\alpha dp_\alpha + p_\alpha d\dot{q}_\alpha) - d\mathcal{L} = \sum_\alpha (\dot{q}_\alpha dp_\alpha - \dot{p}_\alpha dq_\alpha) - \frac{\partial \mathcal{L}}{\partial t} dt \tag{1.99}$$

where in the last step we use Eq. (1.97). Moreover, the following relation holds as well

$$dH = \sum_\alpha \left(\frac{\partial H}{\partial q_\alpha} dq_\alpha + \frac{\partial H}{\partial p_\alpha} dp_\alpha \right) + \frac{\partial H}{\partial t} dt. \tag{1.100}$$

By equating the differentials, we obtain the **Hamilton's equations**

$$\boxed{\dot{p}_\alpha = -\frac{\partial H}{\partial q_\alpha}, \qquad \dot{q}_\alpha = \frac{\partial H}{\partial p_\alpha}, \qquad \frac{\partial H}{\partial t} = -\frac{\partial \mathcal{L}}{\partial t}} \tag{1.101}$$

These are first-order differential equations in time for $2M$ functions, namely the set of degrees of freedom $\{q\}$ and their conjugate momenta $\{p\}$. Therefore, to use this formulation, one needs to (1) write the Lagrangian, (2) calculate the conjugate momenta and express the velocities $\{\dot{q}\}$ in terms of $\{q\}$ and $\{p\}$, (3) perform the Legendre transform of $\mathcal{L}$ to obtain H, and finally (4) use H to write down the Hamilton's equations.

The Hamiltonian formulation of classical mechanics is particularly useful for generalizing the fifth postulate of quantum mechanics. However, before doing so, we want to demonstrate that the Hamiltonian is, under certain conditions, indeed the energy of the system. The Lagrangian $\mathcal{L}$ is the difference between the kinetic energy and the function U. If the latter does not depend on velocities, then it coincides with the potential energy V of the system:

$$\frac{\partial U}{\partial \dot{q}_\alpha} = 0 \qquad \Rightarrow \qquad U = V(\{q\}). \tag{1.102}$$

In fact, from Eq. (1.72), we have $\mathbf{F} = -\nabla U$, and therefore the work done to move the particle from one point $\mathbf{r}$ to another point $\mathbf{r}'$ does not depend on the path. Now let's turn to the kinetic energy T. Since $\mathbf{v} = \sum_\alpha \frac{\partial \mathbf{r}}{\delta q_\alpha} \dot{q}_\alpha$, as seen in Eq. (1.68), we have

$$T = \frac{m}{2} \sum_{\mu\nu} \frac{\partial \mathbf{r}}{\partial q_\mu} \cdot \frac{\partial \mathbf{r}}{\partial q_\nu} \dot{q}_\mu \dot{q}_\nu, \tag{1.103}$$

from which we infer that

$$p_\alpha = \frac{\partial \mathcal{L}}{\partial \dot{q}_\alpha} = \frac{\partial T}{\partial \dot{q}_\alpha} = m \sum_\mu \frac{\partial \mathbf{r}}{\partial q_\alpha} \cdot \frac{\partial \mathbf{r}}{\partial q_\mu} \dot{q}_\mu. \tag{1.104}$$

Here, we have taken into account that by assumption U is independent of velocities. Substituting this result into Eq. (1.98), we find

$$H = m \sum_{\mu\alpha} \frac{\partial \mathbf{r}}{\partial q_\alpha} \cdot \frac{\partial \mathbf{r}}{\partial q_\mu} \dot{q}_\alpha \dot{q}_\mu - \frac{m}{2} \sum_{\mu\nu} \frac{\partial \mathbf{r}}{\partial q_\mu} \cdot \frac{\partial \mathbf{r}}{\partial q_\nu} \dot{q}_\mu \dot{q}_\nu + V = T + V. \tag{1.105}$$

So, to summarize, the Hamiltonian coincides with the energy of the system if the forces are conservative.

It's easy to show that if the potential energy V doesn't explicitly depend on time, then, as it should, the energy is conserved. Indeed,

$$\frac{dH}{dt} = \sum_\alpha \left(\frac{\partial H}{\partial q_\alpha} \dot{q}_\alpha + \frac{\partial H}{\partial p_\alpha} \dot{p}_\alpha \right) = \sum_\alpha (-\dot{p}_\alpha \dot{q}_\alpha + \dot{q}_\alpha \dot{p}_\alpha) = 0, \tag{1.106}$$

where in the last step we use the Hamilton's equations.

1.5.4 Symmetries and Conservation Laws—Poisson Bracket

In physics, there exists a close connection between the symmetries of the Hamiltonian and conservation laws. What is meant by symmetry? We have seen that the Hamiltonian, denoted as $H = H(\{p\}, \{q\}, t)$, is a function of the system's degrees of freedom and their conjugate momenta. Under an infinitesimal variation of both, i.e., $p_\alpha \to p_\alpha + \delta p_\alpha$ and $q_\alpha \to q_\alpha + \delta q_\alpha$, the Hamiltonian changes by the amount

$$\delta H = \sum_\alpha \left(\frac{\partial H}{\partial q_\alpha} \delta q_\alpha + \frac{\partial H}{\partial p_\alpha} \delta p_\alpha \right). \tag{1.107}$$

The changes for which $\delta H = 0$ are referred to as a **symmetry of** H. For instance, in the case of a free particle (thus in the absence of an external potential), $H = \frac{p^2}{2m}$ and therefore the variations $\delta p = 0$ and $\delta q = \epsilon$ (with ϵ infinitesimal) form a symmetry because in this case, $\delta H = 0$. Any infinitesimal variation of $\{p\}$ and $\{q\}$ can be expressed in terms of an infinitesimal parameter ϵ and a function $G(\{p\}, \{q\}, t)$, known as the **generating function**, in the following way

$$\delta p_\alpha = -\epsilon \frac{\partial G}{\partial q_\alpha}, \qquad \delta q_\alpha = \epsilon \frac{\partial G}{\partial p_\alpha}. \tag{1.108}$$

For the previous example with $\delta p = 0$ and $\delta q = \epsilon$, the function $G = p$. Substituting Eq. (1.108) into Eq. (1.107), we find

$$\delta H = \epsilon \sum_\alpha \left(\frac{\partial H}{\partial q_\alpha} \frac{\partial G}{\partial p_\alpha} - \frac{\partial H}{\partial p_\alpha} \frac{\partial G}{\partial q_\alpha} \right) \equiv \epsilon \{H, G\}, \tag{1.109}$$

where we have defined the **Poisson bracket** for two arbitrary functions $f_1(\{p\}, \{q\}, t)$ and $f_2(\{p\}, \{q\}, t)$ as

$$\boxed{\{f_1, f_2\} \equiv \sum_\alpha \left(\frac{\partial f_1}{\partial q_\alpha} \frac{\partial f_2}{\partial p_\alpha} - \frac{\partial f_1}{\partial p_\alpha} \frac{\partial f_2}{\partial q_\alpha} \right) = -\{f_2, f_1\}} \tag{1.110}$$

We can then say that if the generating function G has a zero Poisson bracket with the Hamiltonian H, then the variation generated by G is a symmetry since $\delta H = 0$. Now, let's assume we calculate the generating function G along a physical trajectory, meaning for values of $\{p\}$ and $\{q\}$ that satisfy the Hamilton's equations. We have

$$\begin{aligned} \frac{dG}{dt} &= \sum_\alpha \left(\frac{\partial G}{\partial q_\alpha} \dot{q}_\alpha + \frac{\partial G}{\partial p_\alpha} \dot{p}_a \right) + \frac{\partial G}{\partial t} = \sum_\alpha \left(\frac{\partial G}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha} - \frac{\partial G}{\partial p_\alpha} \frac{\partial H}{\partial q_\alpha} \right) + \frac{\partial G}{\partial t} \\ &= -\{H, G\} + \frac{\partial G}{\partial t} \end{aligned} \tag{1.111}$$

We can conclude that if G generates a symmetry (thus $\{H, G\} = 0$) and if G does not explicitly depend on time (hence $\frac{\partial G}{\partial t} = 0$), then G does not change over time, or in other words, the quantity G is conserved: $\frac{dG}{dt} = 0$. In the example of a free particle, $G = p$ is a symmetry, and thus momentum is a conserved quantity. This is a beautiful property of all the laws of physics: *if a quantity is conserved over time, then the system is invariant under a certain transformation.*

Poisson brackets are particularly simple when we choose the functions f_1 and f_2 to be one a degree of freedom, i.e., $f_1 = q_\mu$, and the other a conjugate momentum, i.e., $f_2 = p_\nu$. In this case, we have

$$\{q_\mu, p_\nu\} = \sum_\alpha \left(\frac{\partial q_\mu}{\partial q_\alpha} \frac{\partial p_\nu}{\partial p_\alpha} - \frac{\partial q_\mu}{\partial p_\alpha} \frac{\partial p_\nu}{\partial q_\alpha} \right) = \sum_\alpha \delta_{\mu\alpha} \delta_{\nu\alpha} = \delta_{\mu\nu}. \tag{1.112}$$

If, on the other hand, both functions are either both degrees of freedom or both conjugate momenta, we have

$$\{q_\mu, q_\nu\} = \{p_\mu, p_\nu\} = 0. \tag{1.113}$$

1.6 The Sixth Postulate

The sixth and final postulate of quantum mechanics is known as the **Dirac postulate**, which allows us to calculate scalar products between eigenstates of one observable and those of another. As seen, based on the third postulate, to each observable, a Hermitian operator is associated. Consider a system characterized by the degrees of freedom $\{q\}$, and let $\{p\}$ be their conjugate momenta. In quantum mechanics, we associate each q_α with a Hermitian operator $\hat{q}_\alpha$ and each p_β with a Hermitian operator $\hat{p}_\beta$. According to the **sixth postulate**, these operators must satisfy the following commutation rules:

SIXTH POSTULATE:

$$\boxed{\hat{q}_\alpha \hat{p}_\beta - \hat{p}_\beta \hat{q}_\alpha = [\hat{q}_\alpha, \hat{p}_\beta] = \mathrm{i}\hbar\delta_{\alpha\beta}} \tag{1.114}$$

$$\boxed{[\hat{q}_\alpha, \hat{q}_\beta] = [\hat{p}_\alpha, \hat{p}_\beta] = 0} \tag{1.115}$$

with $\hbar$ being the Planck constant. In other words, the Poisson brackets of classical mechanics are replaced by a commutator, and the Kronecker delta is multiplied by the factor $\mathrm{i}\hbar$. Degrees of freedom commute with their conjugate momenta only when the Planck constant $\hbar$ is zero. As we see, the results of quantum mechanics reduce to those of classical mechanics in the limit $\hbar \to 0$.

Thanks to the sixth postulate, we can practically compute everything. Let's start with an example. Consider a particle in one dimension, and denote by x its coordinate and by p its conjugate momentum. The quantum operators associated with these observables are the **position operator** and the **momentum operator**, see Eqs. (1.58) and (1.59),

$$\boxed{\hat{x} = \int dx\, x|x\rangle\langle x|, \qquad \hat{p} = \int dp\, p|p\rangle\langle p|} \tag{1.116}$$

with scalar product $\langle x|x'\rangle = \delta(x - x')$ and $\langle p|p'\rangle = \delta(p - p')$. We are here assuming that the spectrum, that is, the possible measurable values, is continuous for both cases. This assumption is supported by numerous experimental pieces of evidence. Now, since both $\{|x\rangle\}$ and $\{|p\rangle\}$ form a basis for the same Hilbert space $\mathcal{H}$, we can expand one in terms of the other. From Eq. (1.61)

$$|p\rangle = \int dx\, \langle x|p\rangle |x\rangle, \qquad |x\rangle = \int dp\, \langle p|x\rangle |p\rangle. \tag{1.117}$$

But what is the value of the scalar product $\langle x|p\rangle$? Clearly, without this information, we cannot perform either the change of basis or calculate many quantities of interest. For example, let's suppose we measure the momentum and obtain the value p. The particle then collapses into the state $|p\rangle$. If we are interested in the probability density of finding the particle at position x immediately after the measurement, according to the fourth postulate, we should calculate $|\langle x|p\rangle|^2$. The knowledge of these scalar products is thus fundamental; without them, quantum mechanics would be an incomplete theory. The sixth postulate precisely serves to fill this gap. Let's see how to proceed.

We define the commutator

$$\hat{Q}_n = [\hat{x}, \hat{p}^n]. \tag{1.118}$$

Using the identity $[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]$ with $\hat{A} = \hat{x}$, $\hat{B} = \hat{p}$ and $\hat{C} = \hat{p}^{n-1}$ we find

$$\begin{aligned}\hat{Q}_n &= \mathrm{i}\hbar\hat{p}^{n-1} + \hat{p}\hat{Q}_{n-1} \\ &= \mathrm{i}\hbar\hat{p}^{n-1} + \hat{p}\left(\mathrm{i}\hbar\hat{p}^{n-2} + \hat{p}\hat{Q}_{n-2}\right) = 2\mathrm{i}\hbar\hat{p}^{n-1} + \hat{p}^2\left(\mathrm{i}\hbar\hat{p}^{n-3} + \hat{p}\hat{Q}_{n-3}\right) \\ &= \cdots = (n-1)\mathrm{i}\hbar\hat{p}^{n-1} + \hat{p}^{n-1}\hat{Q}_1 = n\mathrm{i}\hbar\hat{p}^{n-1}.\end{aligned} \tag{1.119}$$

Let us now act with the operator $\hat{x}$ on the ket $e^{-\frac{\mathrm{i}a\hat{p}}{\hbar}}|x\rangle$

$$\begin{aligned}\hat{x}e^{-\frac{\mathrm{i}a\hat{p}}{\hbar}}|x\rangle &= \sum_{n=0}^{\infty}\frac{1}{n!}\left(-\frac{\mathrm{i}a}{\hbar}\right)^n \hat{x}\hat{p}^n|x\rangle = \sum_{n=0}^{\infty}\frac{1}{n!}\left(-\frac{\mathrm{i}a}{\hbar}\right)^n\left(\hat{Q}_n + \hat{p}^n\hat{x}\right)|x\rangle \\ &= \left(-\frac{\mathrm{i}a}{\hbar}\right)\mathrm{i}\hbar\sum_{n=1}^{\infty}\frac{1}{(n-1)!}\left(-\frac{\mathrm{i}a}{\hbar}\right)^{n-1}\hat{p}^{n-1}|x\rangle + xe^{-\frac{\mathrm{i}a\hat{p}}{\hbar}}|x\rangle \\ &= (x+a)e^{-\frac{\mathrm{i}a\hat{p}}{\hbar}}|x\rangle.\end{aligned} \tag{1.120}$$

The ket $e^{-\frac{\mathrm{i}a\hat{p}}{\hbar}}|x\rangle$ is therefore proportional to the eigenket of the position operator with eigenvalue $(x+a)$, namely

$$e^{-\frac{\mathrm{i}a\hat{p}}{\hbar}}|x\rangle = C|x+a\rangle. \tag{1.121}$$

It is immediately apparent that $C = 1$ because, as the operator $\hat{p}$ is Hermitian, the operator $e^{-\frac{\mathrm{i}a\hat{p}}{\hbar}}$ is unitary and thus does not affect the normalization. Indeed, by taking the scalar product of both sides of the equation above with themselves, we find

$$\langle x|e^{\frac{\mathrm{i}a\hat{p}}{\hbar}}e^{\frac{-\mathrm{i}a\hat{p}}{\hbar}}|x\rangle = \langle x|x\rangle = \delta(0) = |C|^2\langle x+a|x+a\rangle = |C|^2\delta(0). \tag{1.122}$$

Therefore

$$e^{-\frac{\mathrm{i}a\hat{p}}{\hbar}}|x\rangle = |x+a\rangle. \tag{1.123}$$

Now let's take the scalar product of this equation with an eigenket of the momentum operator. This yields

$$e^{-\frac{\mathrm{i}ap}{\hbar}}\langle p|x\rangle = \langle p|x+a\rangle. \tag{1.124}$$

This identity holds for every x and every a. Setting $a = -x$

$$e^{\frac{\mathrm{i}px}{\hbar}}\langle p|x\rangle = \langle p|0\rangle \qquad \Rightarrow \qquad \langle p|x\rangle = e^{-\frac{\mathrm{i}px}{\hbar}}\langle p|0\rangle\,. \tag{1.125}$$

To determine $\langle p|0\rangle$ we use that $\langle p|p'\rangle = \delta(p-p')$ and $\int dx\, |x\rangle\langle x| = 1$:

$$\begin{aligned}\delta(p-p') = \langle p|p'\rangle &= \int dx\, \langle p|x\rangle\langle x|p'\rangle = \int dx\, e^{-\frac{\mathrm{i}(p-p')x}{\hbar}}\langle p|0\rangle\langle 0|p'\rangle \\ &= 2\pi\delta\left(\frac{p-p'}{\hbar}\right)|\langle p|0\rangle|^2 \\ &= 2\pi\hbar\,\delta(p-p')|\langle p|0\rangle|^2 \end{aligned} \tag{1.126}$$

from which it follows that $\langle p|0\rangle = \frac{1}{\sqrt{2\pi\hbar}}$. In deriving Eq. (1.126), we use the following representation of the Dirac delta:

$$\int_{-\infty}^{\infty} dx\, e^{\mathrm{i}\alpha x} = 2\pi\delta(\alpha), \tag{1.127}$$

along with the property $\delta(\beta\alpha) = \delta(\alpha)/|\beta| = \delta(\beta)/|\alpha|$, see Appendix A. This leads us to the important result

$$\boxed{\langle p|x\rangle = \frac{e^{-\frac{\mathrm{i}px}{\hbar}}}{\sqrt{2\pi\hbar}}} \tag{1.128}$$

For a system with M degrees of freedom, a possible basis for the Hilbert space $\mathcal{H}$ is formed by the set of kets $|\{q\}\rangle = |q_1 \dots q_M\rangle$, which are simultaneous eigenkets of all the operators $\hat{q}_\alpha$ with eigenvalue q_α:

$$\hat{q}_\alpha|q_1 \dots q_M\rangle = q_\alpha|q_1 \dots q_M\rangle. \tag{1.129}$$

Indeed, all the operators $\hat{q}_\alpha$ commute with each other, see Eq. (1.115), and therefore they are simultaneously diagonalizable on an orthonormal basis

$$\langle q_1 \dots q_M|q_1' \dots q_M'\rangle = \delta(q_1-q_1')\delta(q_2-q_2')\dots\delta(q_M-q_M'). \tag{1.130}$$

It's important to appreciate the physics hidden behind this scalar product. If we had detectors to measure the observables $\hat{q}_1$, ..., $\hat{q}_M$, then the ket $|q_1 \dots q_M\rangle \in \mathcal{H}$ corresponds to the system's state when all these detectors simultaneously measure and yield the values $q_1 \dots q_M$. If the system is described by the ket $|\Psi\rangle \in \mathcal{H}$, according to the fourth postulate, the probability for this measurement to occur is

$$P(q_1, \dots, q_M) = |\langle q_1 \dots q_M|\Psi\rangle|^2. \tag{1.131}$$

It follows that the probability for the system to have degrees of freedom $q'_1, \dots, q'_M$ immediately after the measurement is zero unless $q'_1 = q_1, \dots, q'_M = q_M$. The Dirac deltas in Eq. (1.130) precisely express this fact. The reason why Dirac deltas appear and not Kronecker deltas is connected to the fact that the spectra of the operators $\hat{q}_1$, ..., $\hat{q}_M$ are continuous, as discussed in Sect. 1.4. As in the case of a single degree of freedom, Eq. (1.130) also tells us how to generalize the resolution of the identity:

$$\hat{\mathbb{1}} = \int dq_1 \dots dq_M |q_1 \dots q_M\rangle\langle q_1 \dots q_M|. \tag{1.132}$$

One can easily convince oneself of the correctness of this equation by multiplying both sides by $|q'_1 \dots q'_M\rangle$ and using Eq. (1.130).

Alternatively, instead of the basis $|q_1 \dots q_M\rangle$, we could choose as a basis the set of kets $|\{p\}\rangle = |p_1 \dots p_M\rangle \in \mathcal{H}$, which are simultaneous eigenkets of all the operators $\hat{p}_\alpha$ with eigenvalue p_α:

$$\hat{p}_\alpha |p_1 \dots p_M\rangle = p_\alpha |p_1 \dots p_M\rangle. \tag{1.133}$$

Indeed, the operators $\hat{p}_\alpha$ also commute with each other, and therefore they are simultaneously diagonalizable on an orthonormal basis

$$\langle p_1 \dots p_M|p'_1 \dots p'_M\rangle = \delta(p_1 - p'_1)\delta(p_2 - p'_2) \dots \delta(p_M - p'_M), \tag{1.134}$$

from which follows the resolution of the identity in the momentum basis

$$\hat{\mathbb{1}} = \int dp_1 \dots dp_M |p_1 \dots p_M\rangle\langle p_1 \dots p_M|. \tag{1.135}$$

More generally, we can construct a basis from the simultaneous eigenkets $|O_1 \dots O_M\rangle \in \mathcal{H}$ of M independent observables $\hat{O}_\alpha$ that all commute with each other. For example, if we have a system with three degrees of freedom, the observables $\hat{q}_1$, $\hat{p}_2$, $\hat{q}_3$ all commute with each other, and therefore a possible basis is the set of kets $|q_1 p_2 q_3\rangle$.

The calculation of the scalar product between a ket $|q_1 \dots q_M\rangle$ (eigenket of the operators $\hat{q}_\alpha$) and a ket $|p_1 \dots p_M\rangle$ (eigenket of the operators $\hat{p}_\alpha$) is carried out in the same way as we did for the case of a single degree of freedom. Using the same manipulations, we have

$$\begin{aligned}\hat{q}_\alpha e^{-\mathrm{i}\sum_\mu \frac{a_\mu \hat{p}_\mu}{\hbar}}|q_1 \dots q_M\rangle &= \prod_{\mu\neq\alpha} e^{-\mathrm{i}\frac{a_\mu \hat{p}_\mu}{\hbar}} \hat{q}_\alpha e^{-\mathrm{i}\frac{a_\alpha \hat{p}_\alpha}{\hbar}}|q_1 \dots q_M\rangle \\ &= (q_\alpha + a_\alpha) e^{-\mathrm{i}\sum_\mu \frac{a_\mu \hat{p}_\mu}{\hbar}}|q_1 \dots q_M\rangle. \end{aligned} \tag{1.136}$$

Since this relation holds for every α, we conclude that

$$e^{-\mathrm{i}\sum_\mu \frac{a_\mu \hat{p}_\mu}{\hbar}}|q_1 \dots q_M\rangle = |q_1 + a_1 \dots q_M + a_M\rangle. \tag{1.137}$$

Taking the scalar product with $\langle p_1 \dots p_M|$ and evaluating everything at $a_\mu = -q_\mu$

$$e^{\mathrm{i}\sum_\mu \frac{q_\mu p_\mu}{\hbar}}\langle p_1 \dots p_M|q_1 \dots q_M\rangle = \langle p_1 \dots p_M|0 \dots 0\rangle. \tag{1.138}$$

Then, using Eq. (1.134) along with Eq. (1.132)

$$\begin{aligned}\delta(p_1 - p_1') \dots \delta(p_M - p_M') &= \int dq_1 \dots dq_M \langle p_1 \dots p_M|q_1 \dots q_M\rangle\langle q_1 \dots q_M|p_1' \dots p_M'\rangle \\ &= \int dq_1 \dots dq_M e^{-\mathrm{i}\sum_\mu \frac{q_\mu(p_\mu - p_\mu')}{\hbar}}\langle p_1 \dots p_M|0 \dots 0\rangle\langle 0 \dots 0|p_1' \dots p_M'\rangle \\ &= (2\pi\hbar)^M \delta(p_1 - p_1') \dots \delta(p_M - p_M')|\langle p_1 \dots p_M|0 \dots 0\rangle|^2. \end{aligned} \tag{1.139}$$

We conclude that $\langle p_1 \dots p_M|0 \dots 0\rangle = 1/\sqrt{(2\pi\hbar)^M}$ and hence

$$\langle p_1 \dots p_M|q_1 \dots q_M\rangle = \frac{1}{\sqrt{(2\pi\hbar)^M}} e^{-\mathrm{i}\sum_\mu \frac{q_\mu p_\mu}{\hbar}}. \tag{1.140}$$

For $M = 1$, this result correctly reduces to Eq. (1.128). For a particle in three dimensions with coordinates $\mathbf{r} = (x, y, z)$, we have

$$\boxed{\langle \mathbf{p}|\mathbf{r}\rangle = \langle p_x p_y p_z|xyz\rangle = \frac{1}{\sqrt{(2\pi\hbar)^3}} e^{-\mathrm{i}\frac{\mathbf{p}\cdot\mathbf{r}}{\hbar}}} \tag{1.141}$$

1.7 Generalization of the Fifth Postulate: Schrödinger Equation

The fifth postulate was stated in Sect. 1.2, essentially consisting of the Schrödinger equation. However, when it was introduced, we didn't yet have the tools to construct the energy operator for a general system with M degrees of freedom. Now we have all the tools. Let $H(\{q\}, \{p\}, t)$ be the Hamiltonian of a system with M degrees of freedom. Given $|\Psi_0\rangle \in \mathcal{H}$ as the ket describing the system at time zero, the evolution of this ket is governed by the **Schrödinger equation**

$$\boxed{\mathrm{i}\hbar\frac{d}{dt}|\Psi(t)\rangle = H(\{\hat{q}\},\{\hat{p}\},t)|\Psi(t)\rangle \equiv \hat{H}(t)|\Psi(t)\rangle} \tag{1.142}$$

with the initial condition $|\Psi(0)\rangle = |\Psi_0\rangle$. Note that $\hat{H}(t) \equiv H(\{\hat{q}\},\{\hat{p}\},t)$ is an operator since the function H is a function of operators. In the case of conservative forces, like the Coulomb force, H is indeed the energy of the system. As we see, the Hamiltonian is always a Hermitian operator.

From the Schrödinger equation follows an important theorem concerning the time dependence of the expectation values of observables. Consider a general observable $\hat{O}$. If the system is described by the ket $|\Psi(t)\rangle$ at time t, its expectation value at this time is given by $\langle\Psi(t)|\hat{O}|\Psi(t)\rangle$. Therefore, the temporal variation of the expectation value is

$$\begin{aligned}\frac{d}{dt}\langle\Psi(t)|\hat{O}|\Psi(t)\rangle &= \left(\frac{d}{dt}\langle\Psi(t)|\right)\hat{O}|\Psi(t)\rangle + \langle\Psi(t)|\hat{O}\left(\frac{d}{dt}|\Psi(t)\rangle\right)\\ &= \frac{\mathrm{i}}{\hbar}\langle\Psi(t)|\left[\hat{H}(t),\hat{O}\right]|\Psi(t)\rangle\end{aligned} \tag{1.143}$$

meaning it is equal to $\mathrm{i}/\hbar$ times the expectation value of the commutator between the Hamiltonian and the operator itself. This result is known as the **Ehrenfest theorem**.

Let's now discuss a case that is encountered frequently, namely that of a time-independent Hamiltonian. Let $\hat{H}(t) = \hat{H}$ and denote by $|E,k\rangle$ the set of its eigenkets with eigenvalue E:

$$\hat{H}|E,k\rangle = E|E,k\rangle. \tag{1.144}$$

In general, there can exist multiple eigenkets with the same eigenvalue, and consequently, there can be multiple values for the index k. Let's delve deeper into this point. As a consequence of what has been mentioned below Eq. (1.135), if a system has M degrees of freedom, we can always find $M-1$ observables $\hat{O}_2,\ldots,\hat{O}_M$ such that the M observables $\hat{H},\hat{O}_2,\ldots,\hat{O}_M$ are all *independent* and *mutually commuting*. For instance, consider a free particle (thus potential energy $V=0$) with mass m in three dimensions, so that $\hat{H} = \frac{\hat{p}^2}{2m}$ with $\hat{p}^2 \equiv \hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2$. A possible choice for the observables $\hat{O}_2, \hat{O}_3$ could be $\hat{p}_y$ and $\hat{p}_z$; indeed, the three observables $\hat{H}, \hat{p}_y, \hat{p}_z$ are mutually independent and commuting. Of course, the observable $\hat{p}_x$ also commutes with $\hat{H}$, so we could equivalently choose the set $\hat{H}, \hat{p}_x, \hat{p}_z$ or the set $\hat{H}, \hat{p}_y, \hat{p}_x$. However, it's not possible to have more than three observables with the desired characteristics. For example, the four observables $\hat{H}, \hat{p}_x, \hat{p}_y, \hat{p}_z$, despite all commuting with each other, are not mutually independent as we can express $\hat{H}$ in terms of $\hat{p}_x, \hat{p}_y, \hat{p}_z$. Let's return to the general case. Since the observables $\hat{H}, \hat{O}_2, \ldots, \hat{O}_M$ commute with each other, there must exist a common basis of eigenkets. Denote by $|E\,O_2\ldots O_M\rangle$ the general common eigenket of $\hat{H}, \hat{O}_2, \ldots, \hat{O}_M$ with eigenvalues $E, O_2, \ldots, O_M$. By virtue of the collapse postulate, we can also give a physical interpretation to this ket: $|E\,O_2\ldots O_M\rangle$ describes the state of the system when a simultaneous measurement of the observables $\hat{H}, \hat{O}_2, \ldots, \hat{O}_M$ yields the values $E, O_2, \ldots, O_M$. It's evident that as $O_2, \ldots, O_M$ vary, the ket $|E O_2 \ldots O_M\rangle$ remains an eigenket of $\hat{H}$ with eigenvalue E. In this case, the index k in Eq. (1.144) is a composite index: $k = (O_2, \ldots, O_M)$. In the previous example of a particle in three dimensions, the eigenvalues of $\hat{H}$ are $E = p_x^2 + p_y^2 + p_z^2$ and if we were to choose the observables $\hat{O}_2, \hat{O}_3$ as $\hat{p}_y$ and $\hat{p}_z$, we can observe that as the eigenvalues p_y and p_z change, the ket $|E p_y p_z\rangle$ remains an eigenket of $\hat{H}$ with eigenvalue E.

We say that the eigenvalue E is **degenerate**, and the degeneracy corresponds to the number of independent eigenstates having that eigenvalue. The state (or states in the case of a degeneracy greater than one) corresponding to the lowest eigenvalue is called the **ground state**. All other states are referred to as **excited states**. The set of eigenvalues of an observable is also known as the **spectrum**. The spectrum of $\hat{H}$ can be discrete, continuous, or it can have both a discrete and a continuous part. The type of spectrum depends on the system. For simplicity, in what follows, we assume that the spectrum of $\hat{H}$ is discrete. The continuous case doesn't introduce any additional difficulties; the only difference is that sums become integrals, and Kronecker deltas become Dirac deltas. We have the opportunity to explore this more thoroughly later on.

Just as the set of kets $|q_1 \ldots q_M\rangle$ or $|p_1 \ldots p_M\rangle$ forms an orthonormal basis for the Hilbert space $\mathcal{H}$, the set of kets $|E, k\rangle$ also forms, according to the third postulate, an orthonormal basis for the same Hilbert space. We have

$$\langle E, k|E', k'\rangle = \delta_{E,E'}\delta_{kk'} \tag{1.145}$$

which implies

$$\sum_{E,k} |E, k\rangle\langle E, k| = 1. \tag{1.146}$$

Let us expand $|\Psi(t)\rangle$ on the eigenkets of $\hat{H}$

$$|\Psi(t)\rangle = \sum_{E,k} c_{E,k}(t)|E, k\rangle. \tag{1.147}$$

Given the orthonormality of the basis, the coefficients are given by $c_{E,k}(t) = \langle E, k|\Psi(t)\rangle$. Therefore, according to the fourth postulate, their squared modulus correspond to the probability of measuring energy E at time t. Obviously, if for a certain energy, the index k can take multiple values, the probability of measuring E is the sum of these probabilities: $P(E) = \sum_k |c_{E,k}(t)|^2$. It's straightforward to verify that $|\Psi(t)\rangle$ satisfies the Schrödinger equation if the coefficients of the expansion depend on time in the following way:

$$c_{E,k}(t) = c_{E,k}(0)e^{-\mathrm{i}\frac{Et}{\hbar}}. \tag{1.148}$$

Indeed

$$\mathrm{i}\hbar\frac{d}{dt}|\Psi(t)\rangle = \sum_{E,k} c_{E,k}(0)e^{-\mathrm{i}\frac{Et}{\hbar}}E|E,k\rangle \tag{1.149}$$

and

$$\hat{H}|\Psi(t)\rangle = \sum_{E,k} c_{E,k}(t)\hat{H}|E,k\rangle = \sum_{E,k} c_{E,k}(0)e^{-\mathrm{i}\frac{Et}{\hbar}}E|E,k\rangle. \tag{1.150}$$

Therefore, the probability of measuring a certain energy is independent of time since $|c_{E,k}(t)|^2 = |c_{E,k}(0)|^2$. The case of the H_2^+ ion analyzed in Sect. 1.2 is a very special case of the general theory just formulated. By using the experimental data that there was a non-zero probability only to measure the two lowest energies of $\hat{H}$, we can set all the coefficients $c_{E,k}(t)$ to zero except for those associated with the two lowest energies. This way, we recover the expansion in Eq. (1.21) and recognize the solution in Eq. (1.25) as a particular case of Eq. (1.148).

Now, let's consider another generic observable $\hat{O}$ with eigenvalues O and eigenstates $|O,i\rangle$ (these eigenstates also form an orthonormal basis for the Hilbert space $\mathcal{H}$, the index i accounts for the degeneracy of the eigenvalue O). The probability of measuring O at time t is given by:

$$P(O) = \sum_i |\langle O,i|\Psi(t)\rangle|^2 = \sum_i \left| \sum_{E,k} c_{E,k}(0)e^{-\mathrm{i}\frac{Et}{\hbar}}\langle O,i|E,k\rangle \right|^2 \tag{1.151}$$

and, in general, it depends on time. Returning once again to the example of the H_2^+ ion, if $|O,i\rangle = |R_1\rangle$ is the (only) eigenstate that describes the electron in R_1 and if the only non-zero coefficients are $c_a(0) = c_b(0) = 1/\sqrt{2}$, then $P(R_1)$ coincides with Eq. (1.33).

The formal solution of the Schrödinger equation for a time-independent Hamiltonian can also be written as:

$$\boxed{|\Psi(t)\rangle = e^{-\mathrm{i}\frac{\hat{H}t}{\hbar}}|\Psi(0)\rangle} \tag{1.152}$$

as can be immediately seen by taking the derivative with respect to time. Therefore, we can also write Eq. (1.151) as:

$$P(O) = \sum_i |\langle O,i|e^{-\mathrm{i}\frac{\hat{H}t}{\hbar}}|\Psi(0)\rangle|^2. \tag{1.153}$$

It's straightforward to verify that this expression coincides with Eq. (1.151) by expanding $|\Psi(0)\rangle$ as in Eq. (1.147). Two observations:

1. If $\hat{O}$ commutes with $\hat{H}$, then we can choose its eigenstates to also be eigenstates of $\hat{H}$. Denoting the energy of the state $|O,i\rangle$ as E_i, we have $\langle O,i|e^{-\mathrm{i}\frac{\hat{H}t}{\hbar}} = \langle O,i|e^{-\mathrm{i}\frac{E_i t}{\hbar}}$, and thus the probability $P(O)$ does not depend on time.

2. If the state $|\Psi_0\rangle$ is an eigenstate of $\hat{H}$ with eigenvalue E, then $e^{-\mathrm{i}\frac{\hat{H}t}{\hbar}}|\Psi_0\rangle = e^{-\mathrm{i}\frac{Et}{\hbar}}|\Psi_0\rangle$, and therefore, even in this case, the probability $P(O)$ does not depend on time. This property holds for all eigenvalues of the operator $\hat{O}$, and thus even the expectation value of the operator, defined in Eq. (1.34), does not depend on time.

We conclude this section with a generalization of the solution to the Schrödinger equation for piecewise constant Hamiltonians. Suppose that at time $t = t_0$ the system is described by the ket $|\Psi(t_0)\rangle$, and the Hamiltonian $\hat{H}(t) = \hat{H}_0$ for all times t in the interval from t_0 to another time $t_1 > t_0$. Then, if $t \in (t_0, t_1)$, the Schrödinger equation in Eq. (1.142) can be written as:

$$\mathrm{i}\hbar\frac{d}{dt}|\Psi(t)\rangle = \hat{H}_0|\Psi(t)\rangle \tag{1.154}$$

which solved by

$$|\Psi(t)\rangle = e^{-\mathrm{i}\frac{\hat{H}_0(t-t_0)}{\hbar}}|\Psi(t_0)\rangle, \qquad t \in (t_0, t_1). \tag{1.155}$$

Indeed, for $t = t_0$ the left-hand side is equal to the right-hand side. Furthermore, if we take the derivative with respect to time, we find precisely Eq. (1.154). It is important to emphasize that Eq. (1.155) represents the state at time t only if $t \in (t_0, t_1)$, given that only within this time interval is the Hamiltonian given by the operator $\hat{H}_0$. Let us now suppose that at time t_1, the Hamiltonian suddenly changes from $\hat{H}_0$ to another operator $\hat{H}_1$, and it remains constant until time $t_2 > t_1$. Then, within the time interval (t_1, t_2), the Schrödinger equation in Eq. (1.142) can be written as:

$$\mathrm{i}\hbar\frac{d}{dt}|\Psi(t)\rangle = \hat{H}_1|\Psi(t)\rangle \tag{1.156}$$

which is solved by

$$|\Psi(t)\rangle = e^{-\mathrm{i}\frac{\hat{H}_1(t-t_1)}{\hbar}}|\Psi(t_1)\rangle, \qquad t \in (t_1, t_2). \tag{1.157}$$

Indeed, for $t = t_1$ the left-hand side is equal to the right-hand side. Furthermore, if we take the derivative with respect to time, we find precisely Eq. (1.156). Once again, let us emphasize that Eq. (1.157) represents the state at time t only if $t \in (t_1, t_2)$, given that only within this time interval is the Hamiltonian given by the operator $\hat{H}_1$. Now, the ket $|\Psi(t_1)\rangle$ can be calculated from Eq. (1.155) by setting $t = t_1$, and thus we can rewrite Eq. (1.157) as:

$$|\Psi(t)\rangle = e^{-\mathrm{i}\frac{\hat{H}_1(t-t_1)}{\hbar}}e^{-\mathrm{i}\frac{\hat{H}_0(t_1-t_0)}{\hbar}}|\Psi(t_0)\rangle, \qquad t \in (t_1, t_2). \tag{1.158}$$

This procedure can be iterated once again, of course. If at time t_2 the Hamiltonian suddenly changes from $\hat{H}_1$ to another operator $\hat{H}_2$ and remains constant until time

$t_3 > t_2$, then within the time interval (t_2, t_3), the Schrödinger equation in Eq. (1.142) can be written as:

$$\mathrm{i}\hbar\frac{d}{dt}|\Psi(t)\rangle = \hat{H}_2|\Psi(t)\rangle \tag{1.159}$$

which is solved by

$$|\Psi(t)\rangle = e^{-\mathrm{i}\frac{\hat{H}_2(t-t_2)}{\hbar}}|\Psi(t_2)\rangle, \qquad t \in (t_2, t_3). \tag{1.160}$$

The ket $|\Psi(t_2)\rangle$ can be computed from Eq. (1.158) by substituting $t = t_2$. This yields:

$$|\Psi(t)\rangle = e^{-\mathrm{i}\frac{\hat{H}_2(t-t_2)}{\hbar}}e^{-\mathrm{i}\frac{\hat{H}_1(t_2-t_1)}{\hbar}}e^{-\mathrm{i}\frac{\hat{H}_0(t_1-t_0)}{\hbar}}|\Psi(t_0)\rangle, \qquad t \in (t_2, t_3). \tag{1.161}$$

At this point, it should be clear how to write the general solution in case the Hamiltonian continues to change in the subsequent time intervals.

1.8 Heisenberg's Uncertainty Principle

In Sect. 1.1, we have observed that having a precise knowledge of the position of the electron in the H_2^+ ion leads to an uncertainty in the value of energy (and therefore momentum), and similarly, having a precise knowledge of the energy leads to an uncertainty in the value of position. In this section, we aim to demonstrate that these empirical observations are rooted in the fact that the position operator $\hat{x}$ and the momentum operator $\hat{p}$ do not commute with each other.

Let us begin by recalling the **Schwarz inequality**. Consider two kets, $|A\rangle$ and $|B\rangle$, belonging to a certain Hilbert space $\mathcal{H}$. Then:

$$\boxed{\langle A|A\rangle\langle B|B\rangle \geq |\langle A|B\rangle|^2} \tag{1.162}$$

The proof is straightforward. Given the property of the scalar product:

$$\big(\langle A| + \lambda^*\langle B|\big)\,(|A\rangle + \lambda|B\rangle) \geq 0, \qquad \forall\lambda. \tag{1.163}$$

Setting $\lambda = -\langle B|A\rangle/\langle B|B\rangle$ the Schwarz inequality is recovered.

Now, let's suppose that our system is described by a normalized ket $|\Psi\rangle$, meaning $\langle\Psi|\Psi\rangle = 1$. The expectation value of two general observables, $\hat{O}_1$ and $\hat{O}_2$, is given by, as seen in Eq. (1.34), $\langle\hat{O}_\xi\rangle = \langle\Psi|\hat{O}_\xi|\Psi\rangle$, where $\xi = 1, 2$. Let's construct two new observables:

$$\hat{\sigma}_{O_\xi} \equiv \hat{O}_\xi - \langle\hat{O}_\xi\rangle, \qquad \xi = 1, 2. \tag{1.164}$$

The expectation value of their square is given by:

$$\langle\hat{\sigma}^2_{O_\xi}\rangle = \langle\hat{O}^2_\xi - 2\hat{O}_\xi\langle\hat{O}_\xi\rangle + \langle\hat{O}_\xi\rangle^2\rangle = \langle\hat{O}^2_\xi\rangle - \langle\hat{O}_\xi\rangle^2 \tag{1.165}$$

and it coincides precisely with the square of the variance defined in Eq. (1.35). The variance provides an indication of how uncertain the measured value is. Let's assume that the system's state is described by the ket $|\Psi\rangle = |O_1\rangle$, meaning it is an eigenket of the operator $\hat{O}_1$ with eigenvalue O_1. In this case, the probability of measuring O_1 is equal to one, and the probability of measuring any other value O_1' is zero. In other words, there is no uncertainty about the measurement outcome. It is then immediately evident that if $|\Psi\rangle = |O_1\rangle$, the variance $\langle\hat{\sigma}^2_{O_1}\rangle$ is zero. Thus, the more certain the measurement value, the smaller the variance; conversely, the more uncertain the value, the larger the variance.

We define the kets

$$|A\rangle = \hat{\sigma}_{O_1}|\Psi\rangle, \qquad |B\rangle = \hat{\sigma}_{O_2}|\Psi\rangle. \tag{1.166}$$

From the Schwarz inequality, we find:

$$\langle\hat{\sigma}^2_{O_1}\rangle\langle\hat{\sigma}^2_{O_2}\rangle \geq \left|\langle\hat{\sigma}_{O_1}\hat{\sigma}_{O_2}\rangle\right|^2. \tag{1.167}$$

Let's express the product of operators $\hat{\sigma}_{O_1}\hat{\sigma}_{O_2}$ as the sum of a Hermitian operator and an anti-Hermitian operator:

$$\hat{\sigma}_{O_1}\hat{\sigma}_{O_2} = \frac{1}{2}\left[\hat{\sigma}_{O_1}, \hat{\sigma}_{O_2}\right] + \frac{1}{2}\left\{\hat{\sigma}_{O_1}, \hat{\sigma}_{O_2}\right\}. \tag{1.168}$$

The first term is a commutator and therefore anti-Hermitian

$$[\hat{\sigma}_{O_1}, \hat{\sigma}_{O_2}]^\dagger = \left(\hat{\sigma}_{O_1}\hat{\sigma}_{O_2} - \hat{\sigma}_{O_2}\hat{\sigma}_{O_1}\right)^\dagger = -[\hat{\sigma}_{O_1}, \hat{\sigma}_{O_2}]. \tag{1.169}$$

The second term is an anticommutator and therefore Hermitian

$$\{\hat{\sigma}_{O_1}, \hat{\sigma}_{O_2}\}^\dagger = \left(\hat{\sigma}_{O_1}\hat{\sigma}_{O_2} + \hat{\sigma}_{O_2}\hat{\sigma}_{O_1}\right)^\dagger = \{\hat{\sigma}_{O_1}, \hat{\sigma}_{O_2}\}. \tag{1.170}$$

Using the fact that the expectation value of a Hermitian operator is real, while the expectation value of an anti-Hermitian operator is purely imaginary, we can rewrite Eq. (1.167) as:

$$\begin{aligned}\langle\hat{\sigma}^2_{O_1}\rangle\langle\hat{\sigma}^2_{O_2}\rangle &\geq \frac{1}{4}\left|\langle[\hat{\sigma}_{O_1}, \hat{\sigma}_{O_2}]\rangle\right|^2 + \frac{1}{4}\left|\langle\{\hat{\sigma}_{O_1}, \hat{\sigma}_{O_2}\}\rangle\right|^2 \\ &\geq \frac{1}{4}\left|\langle[\hat{\sigma}_{O_1}, \hat{\sigma}_{O_2}]\rangle\right|^2.\end{aligned} \tag{1.171}$$

Taking into account the fact that $[\hat{\sigma}_{O_1}, \hat{\sigma}_{O_2}] = [\hat{O}_1, \hat{O}_2]$, we arrive at the **Heisenberg Uncertainty Principle**

$$\boxed{\langle\hat{\sigma}^2_{O_1}\rangle\langle\hat{\sigma}^2_{O_2}\rangle \geq \frac{1}{4}\left|\langle[\hat{O}_1, \hat{O}_2]\rangle\right|^2} \tag{1.172}$$

The Heisenberg Uncertainty Principle translates into mathematical language the fact that if two observables do not commute, then the product of their variances cannot be arbitrarily small, or equivalently, it is not possible to reduce the uncertainty of both measurements simultaneously without limit. Let's consider the case of operators $\hat{O}_1 = \hat{x}$ and $\hat{O}_2 = \hat{p}$. In this case, the commutator $[\hat{x}, \hat{p}] = \mathrm{i}\hbar$, and thus the Heisenberg Uncertainty Principle establishes that

$$\boxed{\langle\hat{\sigma}^2_x\rangle\langle\hat{\sigma}^2_p\rangle \geq \frac{\hbar^2}{4}} \tag{1.173}$$

So, if we are certain about the position, and thus $\langle\hat{\sigma}^2_x\rangle = 0$, the uncertainty in momentum is maximum, $\langle\hat{\sigma}^2_p\rangle \to \infty$. Conversely, if we are certain about the momentum, and thus $\langle\hat{\sigma}^2_p\rangle = 0$, the uncertainty in position is maximum, $\langle\hat{\sigma}^2_x\rangle \to \infty$. In the limit as $\hbar \to 0$, we recover the classical result that both can be known with certainty.

In light of the Heisenberg Uncertainty Principle, we can also understand why the lowest measurable energy value for the electron in the H_2^+ ion is greater than the classical minimum value, as discussed in Sect. 1.1. The classical minimum value is obtained by placing the electron precisely at the bottom of one of the two potential wells with zero momentum. However, quantum mechanically, this situation is impossible since it would imply having absolute certainty in both position and momentum. For such a state, the variances of x and p would be zero, which contradicts the Heisenberg Uncertainty Principle.

1.9 Summary of What We Have Learned So Far

With the previous section, we conclude the first part of the course. Let's briefly summarize the main concepts we have learned so far:

(1) A system with M degrees of freedom is described by the ket $|q_1 \ldots q_M\rangle$ if a simultaneous measurement of these degrees of freedom provides the values $q_1 \ldots q_M$ (collapse postulate).
(2) The set of kets $|q_1 \ldots q_M\rangle$ forms an orthonormal basis of a Hilbert space $\mathcal{H}$.
(3) The most general state $|\Psi\rangle$ that the system can be in is described by a ket belonging to $\mathcal{H}$.
(4) For every observable, there is an associated Hermitian operator, and the possible outcomes of a measurement are the eigenvalues of that operator.

(5) The operators $\hat{q}_\alpha$ associated with the degrees of freedom and the operators $\hat{p}_\alpha$ associated with their conjugate momenta satisfy the commutation rules $[\hat{q}_\alpha, \hat{p}_\beta] = \mathrm{i}\hbar\delta_{\alpha\beta}$ and $[\hat{q}_\alpha, \hat{q}_\beta] = [\hat{p}_\alpha, \hat{p}_\beta] = 0$ (Dirac's postulate), from which it is possible to compute scalar products $\langle p_1 \dots p_M | q_1 \dots q_M \rangle$.

(6) Given M independent observables $\hat{O}_i = O_i(\{\hat{q}\}, \{\hat{p}\})$ that mutually commute, and each with eigenvalues O_i, the ket $|O_1 \dots O_M\rangle$ describes the system's state when a simultaneous measurement of these observables yields the values $O_1, \dots O_M$. Furthermore, the set of kets $|O_1 \dots O_M\rangle$ forms an orthonormal basis of $\mathcal{H}$.

(7) If the system is described by the ket $|\Psi\rangle$, then the probability of measuring $O_1, \dots, O_M$ for the observables $\hat{O}_i$ is given by $P(O_1, \dots, O_M) = |\langle O_1 \dots O_M | \Psi \rangle|^2$, see Eq. (1.131).

(8) The temporal evolution of the ket that describes the system is governed by the Schrödinger equation $\mathrm{i}\hbar\frac{d}{dt}|\Psi(t)\rangle = \hat{H}(t)|\Psi(t)\rangle$, where $\hat{H}(t) = H(\{\hat{q}\}, \{\hat{p}\}, t)$ and H is the Hamiltonian.

In the remaining part of the book, we apply these principles to simple systems and highlight the differences between the quantum and classical descriptions.

1.10 Exercises

1. A particle of mass m is constrained to move on a vertically positioned circle with radius R and is subjected to the force of gravity.
   i. How many degrees of freedom does the particle have?
   ii. Choose the most convenient degrees of freedom and write the Lagrangian of the system.
   iii. Write the Euler-Lagrange equations.
   iv. Calculate the conjugate momentum and write the Hamiltonian in terms of the degrees of freedom and their conjugate momenta.
   v. Write the Hamilton equations.

   Solution *i. One degree of freedom*
   ii. We choose the reference system such that the circle lies in the $y - z$ *plane. In this case, we have* $\mathbf{r} = (0, R\cos\theta, R\sin\theta)$. *The kinetic energy of the particle is then given by* $T = \frac{m}{2}(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) = \frac{mR^2}{2}\dot{\theta}^2$. *The potential energy is* $V(\mathbf{r}) = mgR\sin\theta$. *Therefore, the Lagrangian is* $\mathcal{L}(\theta, \dot{\theta}) = \frac{mR^2}{2}\dot{\theta}^2 - mgR\sin\theta$.
   iii. The Euler-Lagrange equations are $R\ddot{\theta} = -g\cos\theta$.
   iv. The conjugate momentum is $p_\theta = \frac{\partial\mathcal{L}}{\partial\dot{\theta}} = mR^2\dot{\theta}$. *Therefore, the Hamiltonian is* $H(\theta, p_\theta) = \dot{\theta}p_\theta - \mathcal{L} = \frac{p_\theta^2}{2mR^2} + mgR\sin\theta$.
   v. The Hamiltonian equations are $\dot{p}_\theta = -\frac{\partial H}{\partial\theta} = -mgR\cos\theta$ and $\dot{\theta} = \frac{\partial H}{\partial p_\theta} = \frac{p_\theta}{mR^2}$.

2. Let $\hat{a}$ be an operator, not necessarily Hermitian. Among the following six operators, which ones are Hermitian?

$$\hat{A} = (\hat{a}^\dagger)^3\hat{a}^3, \qquad \hat{B} = (\hat{a}^\dagger)^2\hat{a}^2\hat{a}^\dagger\hat{a}, \qquad \hat{C} = \mathrm{i}(\hat{a}^\dagger)^2(\hat{a}^\dagger + \hat{a})\hat{a}^2,$$
$$\hat{D} = \mathrm{i}(\hat{a}^\dagger)^2(\hat{a}^\dagger - \hat{a})\hat{a}^2, \qquad \hat{F} = (\hat{a}^\dagger\hat{a})^3, \qquad \hat{G} = \hat{a}^\dagger\hat{a}(\hat{a}^\dagger - \hat{a})\hat{a}^\dagger\hat{a}$$

Solution $\hat{A}$, $\hat{D}$ *and* $\hat{F}$

3. Consider a Hilbert space of dimension 3, and let $|v_1\rangle$, $|v_2\rangle$, and $|v_3\rangle$ be three mutually orthogonal kets. Among the following operators, which ones are Hermitian?

$$\hat{A} = |v_1\rangle\langle v_2| - \mathrm{i}|v_2\rangle\langle v_1|, \qquad \hat{B} = \mathrm{i}|v_1\rangle\langle v_2| - \mathrm{i}|v_2\rangle\langle v_1|, \qquad \hat{C} = |v_1\rangle\langle v_1| - |v_3\rangle\langle v_3|$$

Solution $\hat{B}$ *and* $\hat{C}$.

4. In a Hilbert space of dimension 2, consider the observable $\hat{A}$ with eigenvalues A_1 and A_2, and orthonormal eigenkets $|A_1\rangle$ and $|A_2\rangle$. Given that:
(1) The probability of measuring A_1 is $\frac{1}{3}$
(2) The expectation value of the observable $\hat{B} = |A_1\rangle\langle A_2| + |A_2\rangle\langle A_1|$ is $\frac{2}{3}$
(3) The expectation value of the observable $\hat{C} = \mathrm{i}|A_1\rangle\langle A_2| - \mathrm{i}|A_2\rangle\langle A_1|$ is $\frac{2}{3}$
Write the normalized ket of the system as a linear combination of $|A_1\rangle$ and $|A_2\rangle$.

Solution *Let* $|\Psi\rangle = \alpha_1|A_1\rangle + \alpha_2|A_2\rangle$ *the sought ket. The normalization* $\langle\Psi|\Psi\rangle = |\alpha_1|^2 + |\alpha_2|^2 = 1$ *implies that we can choose* $\alpha_1 = \cos\theta$ and $\alpha_2 = e^{\mathrm{i}\phi}\sin\theta$ *where* $\theta \in (0, \pi/2)$ *and* $\phi \in (0, 2\pi)$. *According to the the fourth postulate* $P(A_1) = |\langle A_1|\Psi\rangle|^2 = \cos^2\theta = 1/3$. *Therefore* $\cos\theta = 1/\sqrt{3}$ *and consequently* $\sin\theta = \sqrt{2/3}$. *From the second information we have* $\langle\Psi|\hat{B}|\Psi\rangle = \frac{\sqrt{2}}{3}(e^{\mathrm{i}\phi} + e^{-\mathrm{i}\phi}) = 2\frac{\sqrt{2}}{3}\cos\phi = \frac{2}{3}$ *and therefore* $\cos\phi = 1/\sqrt{2}$. *From the third information we have* $\langle\Psi|\hat{C}|\Psi\rangle = \mathrm{i}\frac{\sqrt{2}}{3}(e^{\mathrm{i}\phi} - e^{-\mathrm{i}\phi}) = -2\frac{\sqrt{2}}{3}\sin\phi = \frac{2}{3}$ *and therefore* $\sin\phi = -1/\sqrt{2}$. *We conclude that* $\phi = -\pi/4$. *The solution is then*

$$|\Psi\rangle = \frac{1}{\sqrt{3}}|A_1\rangle + \sqrt{\frac{2}{3}}e^{-\mathrm{i}\pi/4}|A_2\rangle$$

5. Let $|A_1\rangle$ and $|A_2\rangle$ be two orthonormal eigenkets of the observable $\hat{A}$ with eigenvalues A_1 and A_2. Consider the kets $|\Psi\rangle = |A_1\rangle + |A_2\rangle$ and $|\Phi\rangle = -2|A_1\rangle + \mathrm{i}|A_2\rangle$.
i. Calculate the norms $\langle\Psi|\Psi\rangle$ and $\langle\Phi|\Phi\rangle$
ii. Find the condition for the kets $|\Psi\rangle$ and $|\Phi\rangle$ to be eigenkets of $\hat{A}$

Solution *We have* $\langle\Psi|\Psi\rangle = 2$ *and* $\langle\Phi|\Phi\rangle = 5$. *The kets* $|\Psi\rangle$ *and* $|\Phi\rangle$ *are independent and for them to be eigenkets of the observable* $\hat{A}$ *the eigenvalues* A_1 and A_2 *must be identical.*

6. Consider a three-dimensional Hilbert space, and let the energy operator be given by $\hat{E} = \sum_{i=1}^{3} E_i |E_i\rangle\langle E_i|$. The system at time $t = 0$ is described by the ket $|\Psi\rangle$, having the following inner products with the eigenkets of $\hat{E}$:

$$\langle E_1|\Psi\rangle = \frac{1}{\sqrt{2}}, \qquad \langle E_2|\Psi\rangle = \frac{\mathrm{i}}{2}, \qquad \langle E_3|\Psi\rangle = \frac{1}{2},$$

i. Write $|\Psi\rangle$ as a linear combination of the eigenkets of $\hat{E}$.
ii. Calculate the norm $\langle\Psi|\Psi\rangle$.
iii. Write the ket $|\Psi(t)\rangle$ at time t as linear combination of the eigenkets of $\hat{E}$.
iv. Verify that the norm $\langle\Psi(t)|\Psi(t)\rangle$ does not change with time. Why?
v. Given the observable $\hat{A} = |E_2\rangle\langle E_1| + |E_1\rangle\langle E_2| + 2|E_3\rangle\langle E_3|$, calculate the time-dependent average value of the observable at time t, which is $A(t) = \langle\Psi(t)|\hat{A}|\Psi(t)\rangle$.
vi. Calculate the square of the variance at time t, which is $\sigma_A^2(t) = \langle\Psi(t)|\hat{A}^2|\Psi(t)\rangle - A^2(t)$.
vii. Verify that the ket $|\Phi_+\rangle = \frac{1}{\sqrt{2}}(|E_1\rangle + |E_2\rangle)$ is normalized and is an eigenket of $\hat{A}$ with eigenvalue 1. Also, verify that the ket $|\Phi_-\rangle = \frac{1}{\sqrt{2}}(|E_1\rangle - |E_2\rangle)$ is normalized and is an eigenket of $\hat{A}$ with eigenvalue -1. Furthermore, verify that the ket $|E_3\rangle$ is an eigenket of $\hat{A}$ with eigenvalue 2.
viii. Calculate the probability that a measurement of the observable $\hat{A}$ at time t yields the value 1, the probability that it yields the value -1, and the probability that it yields the value 2. Then, verify that the sum of these probabilities adds up to 1.
ix. Verify that the operator $\hat{B} = |\Phi_+\rangle\langle\Phi_+| - |\Phi_-\rangle\langle\Phi_-| + 2|E_3\rangle\langle E_3|$ is the same as the operator $\hat{A}$. Why?

Solution *i. Using the completeness relation* $1 = \sum_{i=1}^{3} |E_i\rangle\langle E_i|$ *we find*

$$|\Psi\rangle = \sum_{i=1}^{3} |E_i\rangle\langle E_i|\Psi\rangle = \frac{1}{\sqrt{2}}|E_1\rangle + \frac{\mathrm{i}}{2}|E_2\rangle + \frac{1}{2}|E_3\rangle$$

ii. $\langle\Psi|\Psi\rangle = \frac{1}{2} + \frac{1}{4} + \frac{1}{4} = 1$
iii. According to Eq. (1.148)

$$|\Psi(t)\rangle = \frac{1}{\sqrt{2}} e^{\mathrm{i}E_1 t}|E_1\rangle + \frac{\mathrm{i}}{2} e^{\mathrm{i}E_2 t}|E_2\rangle + \frac{1}{2} e^{\mathrm{i}E_3 t}|E_3\rangle$$

iv. The normalization does not change with time because the coefficients of the expansion are multiplied by an imaginary exponential, the modulus of which is unity.

v. We have $A(t) = \langle\Psi(t)|E_2\rangle\langle E_1|\Psi(t)\rangle + \langle\Psi(t)|E_1\rangle\langle E_2|\Psi(t)\rangle + 2\langle\Psi(t)|E_3\rangle\langle E_3|\Psi(t)\rangle = -\frac{\mathrm{i}}{2\sqrt{2}}e^{\mathrm{i}(E_1-E_2)t} + \frac{\mathrm{i}}{2\sqrt{2}}e^{-\mathrm{i}(E_1-E_2)t} + \frac{1}{2} = \frac{1}{\sqrt{2}}\sin((E_1-E_2)t) + \frac{1}{2}$.
vi. Taking into account that $\langle E_i|E_j\rangle = \delta_{ij}$ *we have* $\hat{A}^2 = |E_1\rangle\langle E_1| + |E_2\rangle\langle E_2| + 4|E_3\rangle\langle E_3|$. *Therefore* $\langle\Psi|\hat{A}^2|\Psi\rangle = \frac{1}{2} + \frac{1}{4} + 1 = \frac{7}{4}$ *and the variance is* $\sigma_A^2 = \frac{5}{4} - \frac{1}{\sqrt{2}}\sin((E_1-E_2)t)$.
vii. We have $\langle\Phi_+|\Phi_+\rangle = \frac{1}{2} + \frac{1}{2} = 1$ *and similarly* $\langle\Phi_-|\Phi_-\rangle = 1$. Acting on $|\Phi_+\rangle$ *with* $\hat{A}$ *we find*

$$\begin{aligned}\hat{A}|\Phi_+\rangle &= \frac{1}{\sqrt{2}}\Big(|E_2\rangle\langle E_1| + |E_1\rangle\langle E_2| + 2|E_3\rangle\langle E_3|\Big)\Big(|E_1\rangle + |E_2\rangle\Big)\\ &= \frac{1}{\sqrt{2}}\Big(|E_2\rangle + |E_1\rangle\Big) = |\Phi_+\rangle\end{aligned}$$

In a similar way we find $\hat{A}|\Phi_-\rangle = -|\Phi_-\rangle$ *and* $\hat{A}|E_3\rangle = 2|E_3\rangle$.
viii. The probability of finding eigenvalue 1 *at time t is*

$$\begin{aligned}P(1) = |\langle\Psi(t)|\Phi_+\rangle|^2 &= |\frac{1}{2}e^{\mathrm{i}E_1t} + \frac{\mathrm{i}}{2\sqrt{2}}e^{\mathrm{i}E_2t}|^2 = \frac{1}{4}|1 + \frac{\mathrm{i}}{\sqrt{2}}e^{\mathrm{i}(E_2-E_1)t}|^2\\ &= \frac{1}{4}\Big(\frac{3}{2} - \sqrt{2}\sin(E_1-E_2)t)\Big)\end{aligned}$$

With similar manipulations we find $P(-1) = |\langle\Psi(t)|\Phi_-\rangle|^2 = \frac{1}{4}\Big(\frac{3}{2} + \sqrt{2}\sin(E_1-E_2)t)\Big)$ *and* $P(2) = |\langle\Psi(t)|E_3\rangle|^2 = \frac{1}{4}$. *Summing all probabilities* $P(1) + P(-1) + P(2) = 1$ *independent of time.*
ix. The operator $\hat{B}$ *has the same eigenvalues and eigenvectors of the operator* $\hat{A}$. *Therefore they are identical.*

7. Consider a three-dimensional Hilbert space, and let $|v_1\rangle$, $|v_2\rangle$, and $|v_3\rangle$ be three mutually orthonormal kets. Consider the following observables:

$$\hat{A} = |v_1\rangle\langle v_2| + |v_2\rangle\langle v_1| + |v_2\rangle\langle v_3| + |v_3\rangle\langle v_2|$$

$$\hat{B} = -\mathrm{i}|v_1\rangle\langle v_2| + \mathrm{i}|v_2\rangle\langle v_1| - \mathrm{i}|v_2\rangle\langle v_3| + \mathrm{i}|v_3\rangle\langle v_2|$$

i. Calculate the commutator $[\hat{A}, \hat{B}]$. Is it different from zero?
ii. Calculate the square of the variances $\langle\hat{\sigma}_A^2\rangle$ and $\langle\hat{\sigma}_B^2\rangle$ for the state $|\Psi\rangle = |v_2\rangle$. Is it different from zero?
iii. Verify the Heisenberg uncertainty principle.

Solution *i. We have*

$$\hat{A}\hat{B} = \mathrm{i}|v_1\rangle\langle v_1| - \mathrm{i}|v_1\rangle\langle v_3| + \mathrm{i}|v_3\rangle\langle v_1| - \mathrm{i}|v_3\rangle\langle v_3|$$

$$\hat{B}\hat{A} = -\mathrm{i}|v_1\rangle\langle v_1| - \mathrm{i}|v_1\rangle\langle v_3| + \mathrm{i}|v_3\rangle\langle v_1| + \mathrm{i}|v_3\rangle\langle v_3|$$

Therefore $[\hat{A}, \hat{B}] = 2\mathrm{i}|v_1\rangle\langle v_1| - 2\mathrm{i}|v_3\rangle\langle v_3|$.
ii. To calculate the variance we need to calculate the square of the operators. We have

$$\hat{A}^2 = |v_1\rangle\langle v_1| + 2|v_2\rangle\langle v_2| + |v_3\rangle\langle v_3| + |v_1\rangle\langle v_3| + |v_3\rangle\langle v_1|$$

$$\hat{B}^2 = |v_1\rangle\langle v_1| + 2|v_2\rangle\langle v_2| + |v_3\rangle\langle v_3| - |v_1\rangle\langle v_3| - |v_3\rangle\langle v_1|$$

We have $\langle v_2|\hat{A}|v_2\rangle = \langle v_2|\hat{B}|v_2\rangle = 0$. Therefore $\sigma_A^2 = \langle v_2|\hat{A}^2|v_2\rangle = 2$ *and* $\sigma_B^2 = \langle v_2|\hat{B}^2|v_2\rangle = 2$.
iii. Since $\langle v_2|[\hat{A}, \hat{B}]|v_2\rangle = 0$ *the Heisenberg uncertainty principle is satisfied.*

8. In a two-dimensional Hilbert space it is given the operator

$$\hat{A} = -\mathrm{i}|v_1\rangle\langle v_2| + \mathrm{i}|v_2\rangle\langle v_1|$$

where $|v_1\rangle$ and $|v_2\rangle$ form an orthonormal basis.
i. Is the operator $\hat{A}$ Hermitian, unitary, or neither?
ii. Calculate the operator $\hat{C} = \cos(\hat{A})$. Is the operator $\hat{C}$ Hermitian, unitary, or neither?
iii. Calculate the operator $\hat{S} = \sin(\hat{A})$. Is the operator $\hat{S}$ Hermitian, unitary, or neither?
iv. Calculate the operator $\hat{E} = e^{\mathrm{i}\hat{A}}$. Is the operator $\hat{E}$ Hermitian, unitary, or neither?

Solution *i. Since* $\hat{A} = \hat{A}^\dagger$ *the operator is Hermitian.*
ii. Since $\hat{A}^2 = \hat{\mathbb{1}} = |v_1\rangle\langle v_1| + |v_2\rangle\langle v_2|$ we have $\hat{C} = \cos(1)\hat{\mathbb{1}}$, *hence* $\hat{C}$ *is Hermitian.*
iii. For any odd n we have $\hat{A}^n = \hat{A}$ *and therefore* $\hat{S} = \sin(1)\hat{A}$, *which implies that* $\hat{S}$ *is Hermitian.*
iv. We have $\hat{E} = \hat{C} + \mathrm{i}\hat{S} = \cos(1)\hat{\mathbb{1}} + \mathrm{i}\sin(1)\hat{A}$. *We also have* $\hat{E}^\dagger = \cos(1)\hat{\mathbb{1}} - \mathrm{i}\sin(1)\hat{A} \neq \hat{E}$, *and therefore* $\hat{E}$ *is not Hermitian. However* $\hat{E}^\dagger\hat{E} = \hat{\mathbb{1}}$ *and therefore* $\hat{E}$ *is unitary.*

9. In a one-dimensional system, consider the ket $|\Psi\rangle$ with the wave function $\Psi(x) = \langle x|\Psi\rangle = Ce^{-\alpha x^2}$.
i. Determine the constant C such that $\langle\Psi|\Psi\rangle = 1$.
ii. Calculate the average value $\langle\Psi|\hat{A}|\Psi\rangle$ in the case where the observable $\hat{A} = \hat{x} - 1$, in the case where $\hat{A} = \hat{x}^2$, and in the case where $\hat{A} = \delta(\hat{x} - x_0)$, where δ is the Dirac delta function.

Solution *i. Using the completeness relation* $\hat{\mathbb{1}} = \int dx|x\rangle\langle x|$ *we have*

$$\langle\Psi|\Psi\rangle = \int dx \langle\Psi|x\rangle\langle x|\Psi\rangle = \int dx |\Psi(x)|^2 = |C|^2 \int dx e^{-2\alpha x^2} = |C|^2\sqrt{\frac{\pi}{2\alpha}}.$$

Therefore $C = (\frac{2\alpha}{\pi})^{1/4}$.
ii. Using again the completness relation we have $\langle\Psi|\hat{x}-1|\Psi\rangle = \int dx(x-1)|\Psi(x)|^2 = (\frac{2\alpha}{\pi})^{1/2}\int dx\, xe^{-2\alpha x^2} - 1 = -1$. *Similarly we have* $\langle\Psi|\hat{x}^2|\Psi\rangle = (\frac{2\alpha}{\pi})^{1/2}\int dx\, x^2 e^{-2\alpha x^2} = (\frac{2\alpha}{\pi})^{1/2}(\frac{2\alpha}{\pi})^{-1/2}\frac{1}{4\alpha} = \frac{1}{4\alpha}$. *Finally* $\langle\Psi|\delta(\hat{x}-x_0)|\Psi\rangle = |\Psi(x_0)|^2(\frac{2\alpha}{\pi})^{1/2}e^{-2\alpha x_0^2}$.

10. Consider a particle in one dimension, and let's denote its coordinate as x and its conjugate momentum as p. Let $\hat{x}$ and $\hat{p}$ be the corresponding observables, and let $|x\rangle$ and $|p\rangle$ be the corresponding eigenkets. Prove that:

$$e^{-\frac{\mathrm{i}q\hat{x}}{\hbar}}|p\rangle = |p-q\rangle$$

Solution *The proof goes along the same lines as for Eq. (1.123). Hint, show that* $[\hat{p}, \hat{x}^n] = -\mathrm{i}\hbar\hat{x}^{n-1}$.

11. A particle in one dimension is described by the ket $|\Phi\rangle$ such that the scalar product with the eigenkets of position (i.e., the wave function) is $\Phi(x) = \langle x|\Phi\rangle = \sin(kx)$. Calculate the scalar product $\langle p|\Phi\rangle$ of the ket $|\Phi\rangle$ with the eigenkets of the conjugate momentum.

Solution *Using the completeness relation* $\hat{\mathbb{1}} = \int dx|x\rangle\langle x|$ *we have*

$$\langle p|\Phi\rangle = \int dx\langle p|x\rangle\langle x|\Phi\rangle = \frac{1}{\sqrt{2\pi\hbar}}\int dx e^{-\frac{\mathrm{i}px}{\hbar}}\frac{1}{2\mathrm{i}}\left(e^{\mathrm{i}kx} - e^{-\mathrm{i}kx}\right) = -\mathrm{i}\sqrt{\frac{\pi}{2\hbar}}\left[\delta\left(k-\frac{p}{\hbar}\right) - \delta\left(k+\frac{p}{\hbar}\right)\right]$$

where we have used Eq. (1.128) and the representation of the Dirac delta, see Appendix A.

12. Consider a particle in one dimension described by the wave function $\Psi(x) = \delta(x-x_0)$. Which is the ket $|\Psi\rangle$?

Solution $|\Psi\rangle = |x_0\rangle$ *as it follows from the inner product in Eq. (1.54).*

13. Consider a particle in one dimension described by the wave function $\Psi(x) = \langle x|\Psi\rangle = Ce^{-k|x-x_0|}$ with $k > 0$.
i. Find the constant C such that $\langle\Psi|\Psi\rangle = 1$.
ii. Calculate the average position $\langle\Psi|\hat{x}|\Psi\rangle$ and the average of the conjugate momentum $\langle\Psi|\hat{p}|\Psi\rangle$.
iii. Calculate the variance of position $\langle\hat{\sigma}_x^2\rangle$ and of momentum $\langle\hat{\sigma}_p^2\rangle$, and verify that the Heisenberg uncertainty principle is satisfied.

Solution *i. We have* $\langle\Psi|\Psi\rangle = |C|^2 \int_{-\infty}^{\infty} dx |\Psi(x)|^2 = 2\,C|^2 \int_0^{\infty} dx e^{-2kx} = \frac{|C|^2}{k}$. *Therefore* $C = \sqrt{k}$.
ii. The average position is given by

$$\langle\Psi|\hat{x}|\Psi\rangle = k \int\limits_{-\infty}^{\infty} dx(x - x_0 + x_0)e^{-2k|x-x_0|} = k \int\limits_{-\infty}^{\infty} dy y e^{-2k|y|} + x_0 = x_0$$

The average momentum is given by

$$\langle\Psi|\hat{x}|\Psi\rangle = -\mathrm{i}\hbar k \int\limits_{-\infty}^{\infty} dx e^{-k|x-x_0|} \frac{d}{dx} e^{-k|x-x_0|} = 0$$

iii. To calculate the variances we need to calculate the averages of x^2 and p^2. *We have*

$$\langle\Psi|\hat{x}^2|\Psi\rangle = k \int\limits_{-\infty}^{\infty} dx(x - x_0 + x_0)^2 e^{-2k|x-x_0|} = k \int\limits_{-\infty}^{\infty} dy y^2 e^{-2k|y|} + x_0^2 = \frac{1}{2k^2} + x_0^2$$

and therefore $\langle\hat{\sigma}_x^2\rangle = \frac{1}{2k^2}$. *For the momentum variance we have*

$$\begin{aligned}\langle\Psi|\hat{p}^2|\Psi\rangle &= -\hbar^2 k \int\limits_{-\infty}^{\infty} dx e^{-k|x-x_0|} \frac{d^2}{dx^2} e^{-k|x-x_0|} = \hbar^2 k \int\limits_{-\infty}^{\infty} dx \Big[\frac{d}{dx} e^{-k|x-x_0|}\Big]\Big[\frac{d}{dx} e^{-k|x-x_0|}\Big] \\ &= 2\hbar^2 k \int\limits_0^{\infty} dy k^2 e^{-2ky} = \hbar^2 k^2 \qquad (1.174)\end{aligned}$$

and therefore $\langle\hat{\sigma}_p^2\rangle = \hbar^2 k^2$. *We conclude that* $\langle\hat{\sigma}_x^2\rangle\langle\hat{\sigma}_p^2\rangle = \frac{\hbar^2}{2} > \frac{\hbar^2}{4}$, *and hence that the Heisenberg uncertainty principle is satisfied.*

14. In a Hilbert space of dimension 2, the operator is given by

$$\hat{A} = -\mathrm{i}|v_1\rangle\langle v_2| + |v_2\rangle\langle v_1|$$

where $|v_1\rangle$ and $|v_2\rangle$ form an orthonormal basis.
i. The operator $\hat{A}$ is Hermitian, unitary, or neither?
ii. Consider the operator $\hat{B} = \hat{A} - (1 - \mathrm{i})|v_2\rangle\langle v_1|$. Calculate the operator $\hat{E} = e^{\mathrm{i}\hat{B}}$.
iii. Calculate the ket $|\Psi\rangle = \hat{E}|v_1\rangle$ and determine its normalization. Comment on the result.

iv. What are the possible outcomes of a measurement of $\hat{B}$? And what are the probabilities of obtaining these results if the system is in the state $|\Psi\rangle$?

Solution *i. It turns out that* $\hat{A}^\dagger = \mathrm{i}|v_1\rangle\langle v_2| + |v_2\rangle\langle v_1| \neq \hat{A}$, *so* $\hat{A}$ *is not Hermitian. Furthermore,* $\hat{A}\hat{A}^\dagger = -\mathrm{i}|v_1\rangle\langle v_1| + \mathrm{i}|v_2\rangle\langle v_2| \neq \hat{\mathbb{1}} = |v_1\rangle\langle v_1| + |v_2\rangle\langle v_2|$ *and therefore* $\hat{A}$ *is not unitary either.*
ii. The operator $\hat{B} = -\mathrm{i}|v_1\rangle\langle v_2| + \mathrm{i}|v_2\rangle\langle v_1|$ *is Hermitian, and we have* $\hat{B}^2 = \hat{\mathbb{1}}$. *Therefore,* $\hat{E} = \cos(\hat{B}) + \mathrm{i}\sin(\hat{B}) = \cos(1)\nVdash + \mathrm{i}\sin(1)\hat{B}$.
iii. It results in $|\Psi\rangle = \cos(1)|v_1\rangle - \sin(1)|v_2\rangle$. *The normalization is equal to 1, as it should be for a unitary operator* $\hat{E}$.
iv. The possible outcomes of a measurement of $\hat{B}$ *are the eigenvalues of* $\hat{B}$. *The eigenvalues of* $\hat{B}$ *are* $\lambda_+ = 1$ *with eigenvector* $|\phi_+\rangle = \frac{1}{\sqrt{2}}(|v_1\rangle + \mathrm{i}|v_2\rangle)$ *and* $\lambda_- = -1$ *with eigenvector* $|\phi_-\rangle = \frac{1}{\sqrt{2}}(|v_1\rangle - \mathrm{i}|v_2\rangle)$. *Therefore, the probability of measuring* $\lambda_\pm$ *is* $P(\lambda_\pm) = |\langle\Psi|\phi_\pm\rangle|^2 = \frac{1}{2}\,|\cos(1) \mp \mathrm{i}\sin(1)|^2 = \frac{1}{2}$.

Chapter 2
Quantum Systems in Finite-Dimensional Hilbert Spaces

It is much more common than one might imagine that, for a given problem concerning a system with M degrees of freedom, the number of quantum states to consider is not the entire set $|q_1 \dots q_M\rangle$, but only a finite number of states $|\varphi_k\rangle$ (each of which can obviously be expressed as a linear combination of the kets $|q_1 \dots q_M\rangle$). For example, in the case of an electron in the H_2^+ ion, the Hilbert space of the electron is given by the set of eigenkets $|x\rangle$ of the position operator. However, at zero temperature, a good description can be obtained by considering only the kets $|R_1\rangle$ and $|R_2\rangle$. The choice of the set of kets $|\varphi_k\rangle$ is generally dictated by the *system*, the *problem*, and especially our *physical intuition*. In this chapter, we do not discuss how to choose the kets $|\varphi_k\rangle$. Instead, we assume that someone else has done it for us and we here show how to simplify the equations of the previous chapter.

2.1 From Operators to Matrices, from Kets to Column Vectors, from Bras to Row Vectors

Let's assume that the system can only be in a finite number of quantum states $|\varphi_k\rangle$, where $k = 1, \dots, N$. Without loss of generality, we also assume that these states are orthonormal to each other

$$\langle\varphi_k|\varphi_{k'}\rangle = \delta_{kk'}. \tag{2.1}$$

If they are not orthonormal, we can indeed orthogonalize them using, for example, the Gram-Schmidt procedure. The set of these kets forms an orthonormal basis for a Hilbert space $\mathcal{H}'$. From the original Hilbert space $\mathcal{H}$, we are then considering a subspace $\mathcal{H}' \subset \mathcal{H}$. The most general ket in $\mathcal{H}'$ can be written as follows:

$$|\Psi\rangle = \sum_{k=1}^{N} \Psi_k |\varphi_k\rangle, \qquad \Psi_k = \langle\varphi_k|\Psi\rangle. \tag{2.2}$$

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From now on, unless specified otherwise, sums are always understood to range from 1 to N. A generic operator $\hat{O}$, defined in $\mathcal{H}$, when acting on $|\Psi\rangle \in \mathcal{H}' \subset \mathcal{H}$ may not necessarily generate a ket within $\mathcal{H}'$. However, we are not interested in a generic operator. Our working assumptions only make sense for a given system and a specific problem. Therefore, we are interested in operators for which the components of $\hat{O}|\Psi\rangle$ outside of $\mathcal{H}'$ are very small, approaching negligibility in the limit. In such a case,

$$\hat{O}|\Psi\rangle = \sum_k \Psi_k \hat{O}|\varphi_k\rangle \in \mathcal{H}' \tag{2.3}$$

Of course, for this to happen independently of the coefficients Ψ_k, it is necessary that $\hat{O}|\varphi_k\rangle \in \mathcal{H}'$ for all k. Knowing the action of $\hat{O}$ on all the kets of the basis allows us to calculate the action of $\hat{O}$ on a generic ket. What information do we need to determine the action of $\hat{O}$ on the various $|\varphi_k\rangle$? Considering that in $\mathcal{H}'$, the resolution of the identity is written as follows

$$\sum_k |\varphi_k\rangle\langle\varphi_k| = 1, \tag{2.4}$$

we have

$$\hat{O}|\varphi_k\rangle = \sum_{k'} |\varphi_{k'}\rangle\langle\varphi_{k'}|\hat{O}|\varphi_k\rangle = \sum_{k'} O_{k'k}|\varphi_{k'}\rangle. \tag{2.5}$$

Therefore, knowledge of the matrix $\mathbb{O}$ with elements $O_{k'k} \equiv \langle\varphi_{k'}|\hat{O}|\varphi_k\rangle$ is all that is needed. The matrix $\mathbb{O}$ is called the **representation** of the operator $\hat{O}$ in the basis of $|\varphi_k\rangle$. Clearly, the matrix changes if we change the basis. However, since $\hat{O}$ is a Hermitian operator, i.e., $\hat{O}^\dagger = \hat{O}$, the matrix $\mathbb{O}$ is Hermitian regardless of the basis. In fact,

$$O^*_{kk'} = \langle\varphi_k|\hat{O}|\varphi_{k'}\rangle^* = \langle\varphi_{k'}|\hat{O}^\dagger|\varphi_k\rangle = \langle\varphi_{k'}|\hat{O}|\varphi_k\rangle = O_{k'k}. \tag{2.6}$$

Inserting Eq. (2.5) in Eq. (2.3) we find

$$\hat{O}|\Psi\rangle = \sum_{kk'} O_{k'k}\Psi_k|\varphi_{k'}\rangle. \tag{2.7}$$

So the ket $|\Phi\rangle \equiv \hat{O}|\Psi\rangle$ is also a linear combination of the $|\varphi_k\rangle$, as it should be. Let's define the vector $\boldsymbol{\Psi}$ with components Ψ_k and the vector $\boldsymbol{\Phi}$ with components $\Phi_k = \langle\varphi_k|\Phi\rangle$. From now on, we use bold letters (both Greek and Latin) to represent vectors. These vectors are the **representation** of the kets $|\Psi\rangle$ and $|\Phi\rangle$ in the basis of $|\varphi_k\rangle$. Clearly, the vectors change if we change the basis. Note that for a quantum system describing a particle in one dimension, as discussed in Sect. 1.4, the eigenkets $|x\rangle$ of the position operator form a basis of the Hilbert space. If we do not truncate the Hilbert space, i.e., if we take all $|x\rangle$, then the representation of the ket $|\Psi\rangle$ in the basis of $|x\rangle$ is an infinite-dimensional vector with components $\Psi(x) = \langle x|\Psi\rangle$.

In other words, the wave function is nothing but the representation of a ket in the position basis. But let's get back to our discussion. We have

$$|\Phi\rangle = \sum_{k'} |\varphi_{k'}\rangle\langle\varphi_{k'}|\Phi\rangle = \sum_{k'} \Phi_{k'}|\varphi_{k'}\rangle = \sum_{kk'} O_{k'k}\Psi_k|\varphi_{k'}\rangle \tag{2.8}$$

From which it follows that, due to the linear independence of the kets $|\varphi_k\rangle$, $\Phi_{k'} = \sum_k O_{k'k}\Psi_k$. Therefore, the k'-th component of the vector $\mathbf{\Phi}$ is obtained by taking the dot product between the k'-th row of the matrix $\mathbb{O}$ and the vector $\mathbf{\Psi}$. But this means that

$$\boxed{\mathbf{\Phi} = \mathbb{O}\mathbf{\Psi}} \tag{2.9}$$

In other words, the vector $\mathbf{\Phi}$, representing $|\Phi\rangle = \hat{O}|\Psi\rangle$ in the basis $|\varphi_k\rangle$, is the product of the matrix representing $\hat{O}$ and the vector representing $|\Psi\rangle$ in the same basis.

With these premises, we can easily calculate the eigenvectors and eigenvalues of the Hamiltonian in the space $\mathcal{H}'$. Let's suppose we need to solve the problem $\hat{H}|E\rangle = E|E\rangle$. Based on what we have just learned, the vector representing $\hat{H}|E\rangle$ can be written as $\mathbb{H}\mathbf{E}$, where $\mathbb{H}$ is the matrix representing $\hat{H}$ and $\mathbf{E}$ is the vector representing $|E\rangle$. So,

$$\hat{H}|E\rangle = E|E\rangle \qquad \Rightarrow \qquad \mathbb{H}\mathbf{E} = E\mathbf{E} \tag{2.10}$$

Let's denote by $E^{(n)}$ the eigenvalues of $\mathbb{H}$ and by $\mathbf{E}^{(n)}$ its eigenvectors. Since $\mathbb{H}$ is an $N \times N$ matrix, we have N eigenvalues (not necessarily all distinct from each other) and N eigenvectors:

$$\mathbb{H}\mathbf{E}^{(n)} = E^{(n)}\mathbf{E}^{(n)}, \qquad n = 1, \ldots, N \tag{2.11}$$

The eigenkets $|E^{(n)}\rangle$ are simply given by

$$|E^{(n)}\rangle = \sum_k E_k^{(n)}|\varphi_k\rangle \tag{2.12}$$

where $E_k^{(n)}$ is the kth component of the vector $\mathbf{E}^{(n)}$.

Representing operators and kets in a certain basis can be very convenient for carrying out calculations. Often in quantum mechanics problems, the physical meaning of the basis $|\varphi_k\rangle$ is omitted, and representations of operators or kets in a specific basis are written directly. As we have seen, once the basis is fixed, we can easily convert equations written in terms of matrices and vectors into equations written in terms of operators and kets. Conversely, an equation written in terms of operators and kets can be easily converted into an equation for matrices and vectors. But what do we do when we have an equation that contains the product of multiple operators? Or when the equation involves bras?

Consider the product operator $\hat{C} = \hat{A}\hat{B}$. Its representation $\mathbb{C}$ has matrix elements

$$C_{kk'} = \langle\varphi_k|\hat{C}|\varphi_{k'}\rangle = \langle\varphi_k|\hat{A}\hat{B}|\varphi_{k'}\rangle = \sum_p \langle\varphi_k|\hat{A}|\varphi_p\rangle\langle\varphi_p|\hat{B}|\varphi_{k'}\rangle = \sum_p A_{kp}B_{pk}. \tag{2.13}$$

So the matrix $\mathbb{C}$ is simply the product of the matrix $\mathbb{A}$ and the matrix $\mathbb{B}$

$$\boxed{\mathbb{C} = \mathbb{A}\mathbb{B}} \tag{2.14}$$

More generally, if we have a function of operators $F(\hat{A}, \hat{B}, \hat{C}, \ldots) = \hat{F}$, its representation is simply given by the function of matrices

$$\boxed{\mathbb{F} = F(\mathbb{A}, \mathbb{B}, \mathbb{C}, \ldots)} \tag{2.15}$$

Suppose instead we need to calculate the action of an operator on a bra, $\langle\Psi|\hat{O} = \langle\Phi|$. Multiplying the equation by the ket $|\varphi_k\rangle$, we find

$$\langle\Psi|\hat{O}|\varphi_k\rangle = \sum_{k'} \langle\Psi|\varphi_{k'}\rangle\langle\varphi_{k'}|\hat{O}|\varphi_k\rangle = \langle\Phi|\varphi_k\rangle. \tag{2.16}$$

Now, $\langle\Psi|\varphi_{k'}\rangle = \langle\varphi_{k'}|\Psi\rangle^* = \Psi^*_{k'}$ and $\langle\Phi|\varphi_k\rangle = \langle\varphi_k|\Phi\rangle^* = \Phi^*_k$. So, the equation above can also be written as $\sum_{k'} \Psi^*_{k'} O_{k'k} = \Phi^*_k$. On the left-hand side of the equation, we recognize the dot product between a row vector with components $\Psi^*_{k'}$ and the column vector formed by column k of the matrix $\mathbb{O}$. Since this relation must hold for every k, it follows that

$$\langle\Psi|\hat{O} = \langle\Phi| \qquad \Rightarrow \qquad \boxed{\boldsymbol{\Psi}^\dagger\mathbb{O} = \boldsymbol{\Phi}^\dagger} \tag{2.17}$$

So, the representation of the bra $\langle\Psi|$ is the dagger (conjugate transpose) of the vector representing the ket $|\Psi\rangle$.

In conclusion, the representation of an equation written in terms of bras, operators, and kets can be obtained by replacing bras with their representation in terms of row vectors, operators with their representation in terms of matrices, and kets with their representation in terms of column vectors.

2.2 Quantum Systems with Two States—Pauli Matrices

The simplest quantum system is the one for which it is possible to solve a given problem using only two kets, as in the example of the electron in the H_2^+ ion. In this case, all observables are represented by Hermitian 2 × 2 matrices. The most general Hermitian 2 × 2 matrix can be written as

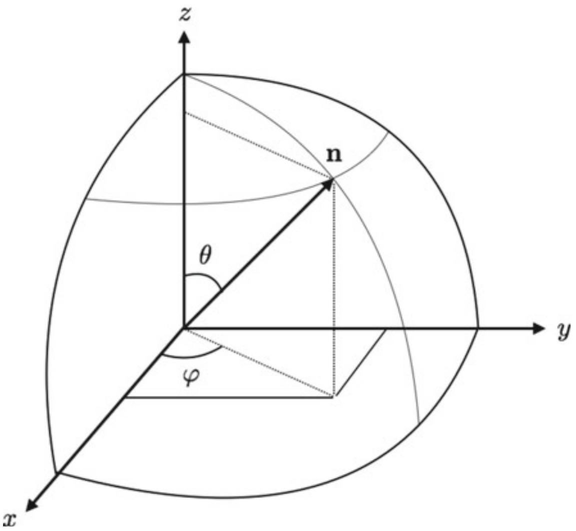

Fig. 2.1 Polar representation of a unit vector

$$\mathbb{O} = \begin{pmatrix} a_0 + a_3 & a_1 - \mathrm{i}a_2 \\ a_1 + \mathrm{i}a_2 & a_0 - a_3 \end{pmatrix} \tag{2.18}$$

where the constants a_0, a_1, a_2, a_3 are all real. It is easy to verify that regardless of the values of these constants, $\mathbb{O} = \mathbb{O}^\dagger$. Introducing the **Pauli matrices**

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{2.19}$$

we can rewrite $\mathbb{O}$ as

$$\mathbb{O} = a_0 \mathbb{1} + a_1\sigma_1 + a_2\sigma_2 + a_3\sigma_3 = a_0 \mathbb{1} + \boldsymbol{a} \cdot \boldsymbol{\sigma} \tag{2.20}$$

where $\mathbb{1}$ is the 2×2 identity matrix, $\boldsymbol{a}$ is the vector with components (a_1, a_2, a_3), and $\boldsymbol{\sigma}$ is the vector of Hermitian matrices $(\sigma_1, \sigma_2, \sigma_3)$. Let's further manipulate Eq. (2.20). Let

$$a = \sqrt{a_1^2 + a_2^2 + a_3^2} \tag{2.21}$$

the magnitude of the vector $\boldsymbol{a}$. The vector $\mathbf{n} = \boldsymbol{a}/a$ is then a unit vector with a magnitude of 1, as shown in Fig. 2.1, and as such, it can always be written as

$$\mathbf{n} = \begin{pmatrix} a_1/a \\ a_2/a \\ a_3/a \end{pmatrix} = \begin{pmatrix} \sin\theta\cos\varphi \\ \sin\theta\sin\varphi \\ \cos\theta \end{pmatrix} \tag{2.22}$$

The angles θ and ϕ can be expressed in terms of a_1, a_2, a_3 by equating the components. For example, from the last component, we obtain that $\theta = \arccos(a_3/a)$, while from the ratio between the second and first component, we obtain that $\phi = \arctan(a_2/a_1)$. Using the expression of $\mathbf{n}$ in terms of the angles θ and ϕ, the matrix $\mathbb{O}$ can be rewritten as:

$$\boxed{\mathbb{O} = a_0 \mathbb{1} + a\mathbf{n} \cdot \boldsymbol{\sigma}} \tag{2.23}$$

where

$$\boxed{\mathbf{n} \cdot \boldsymbol{\sigma} = \begin{pmatrix} \cos\theta & \sin\theta e^{-\mathrm{i}\varphi} \\ \sin\theta e^{\mathrm{i}\varphi} & -\cos\theta \end{pmatrix}} \tag{2.24}$$

Now let's study the matrix $\mathbf{n} \cdot \boldsymbol{\sigma}$. The eigenvalues of $\mathbf{n} \cdot \boldsymbol{\sigma}$ are $\lambda_+ = 1$ and $\lambda_- = -1$, and by using the trigonometric formulas

$$\begin{aligned} \cos(\alpha - \beta) &= \cos\alpha\cos\beta + \sin\alpha\sin\beta \\ \sin(\alpha - \beta) &= \sin\alpha\cos\beta - \cos\alpha\sin\beta \end{aligned} \tag{2.25}$$

it is straightforward to verify that the eigenvectors associated with them are

$$\boxed{\boldsymbol{\psi}_+ = \begin{pmatrix} e^{-\mathrm{i}\varphi/2}\cos(\theta/2) \\ e^{\mathrm{i}\varphi/2}\sin(\theta/2) \end{pmatrix}, \qquad \boldsymbol{\psi}_- = \begin{pmatrix} -e^{-\mathrm{i}\varphi/2}\sin(\theta/2) \\ e^{\mathrm{i}\varphi/2}\cos(\theta/2) \end{pmatrix}} \tag{2.26}$$

The vectors $\boldsymbol{\psi}_+$ and $\boldsymbol{\psi}_-$ are correctly orthogonal as they are associated with distinct eigenvalues of the same Hermitian operator $\mathbf{n} \cdot \boldsymbol{\sigma}$. In particular, both $\boldsymbol{\psi}_+$ and $\boldsymbol{\psi}_-$ are normalized to 1, forming an orthonormal basis. Therefore, the kets associated with them, $|\psi_\pm\rangle$, can be used to write the resolution of the identity as follows:

$$\hat{\mathbb{1}} = |\psi_+\rangle\langle\psi_+| + |\psi_-\rangle\langle\psi_-| \tag{2.27}$$

and based on what we have learned in the previous section, the representation of this equation is

$$\mathbb{1} = \boldsymbol{\psi}_+\boldsymbol{\psi}_+^\dagger + \boldsymbol{\psi}_-\boldsymbol{\psi}_-^\dagger \tag{2.28}$$

since the representation of $\hat{\mathbb{1}}$ is precisely the identity matrix $\mathbb{1}$. Let's emphasize that the vectors $\boldsymbol{\psi}_+$ and $\boldsymbol{\psi}_-$ are two-component vectors as they are eigenvectors of 2×2 matrices. They should be kept distinct from vectors like $\boldsymbol{a}$ or $\mathbf{n}$ which have three components and are used to represent the matrix $\mathbb{O}$.

The eigenvalue equation $(\mathbf{n} \cdot \boldsymbol{\sigma})\boldsymbol{\psi}_\pm = \pm\boldsymbol{\psi}_\pm$ implies that $a(\mathbf{n} \cdot \boldsymbol{\sigma})\boldsymbol{\psi}_\pm = \pm a\boldsymbol{\psi}_\pm$. Therefore

$$\boxed{\mathbb{O}\,\boldsymbol{\psi}_\pm = a_0\mathbb{1}\boldsymbol{\psi}_\pm + a(\mathbf{n} \cdot \boldsymbol{\sigma})\boldsymbol{\psi}_\pm = (a_0 \pm a)\boldsymbol{\psi}_\pm} \tag{2.29}$$

It follows that the vectors ψ_+ and ψ_- are also eigenvectors of the matrix $\mathbb{O}$ with eigenvalues $(a_0 + a)$ and $(a_0 - a)$. Furthermore, for any generic matrix function $F(\mathbb{O})$, we have

$$\boxed{F(\mathbb{O})\,\psi_\pm = F(a_0 \pm a)\psi_\pm} \tag{2.30}$$

Particularly interesting is the evaluation of the unitary matrix $e^{\mathrm{i}\mathbb{O}}$. In fact, in the case where $\mathbb{O} = -\mathbb{H}t/\hbar$, with $\mathbb{H}$ being the Hamiltonian, the matrix in question becomes $e^{-\mathrm{i}\mathbb{H}t/\hbar}$, and as we know, this matrix allows us to determine the temporal evolution. Using Eq. (2.28) and Eq. (2.30), we have

$$e^{\mathrm{i}\mathbb{O}} = e^{\mathrm{i}\mathbb{O}}\mathbb{1} = e^{\mathrm{i}\mathbb{O}}\left(\psi_+\psi_+^\dagger + \psi_-\psi_-^\dagger\right) = e^{\mathrm{i}(a_0+a)}\psi_+\psi_+^\dagger + e^{\mathrm{i}(a_0-a)}\psi_-\psi_-^\dagger\,. \tag{2.31}$$

Let us perform this calculation. We have

$$\begin{aligned}\psi_+\psi_+^\dagger &= \begin{pmatrix} e^{-\mathrm{i}\varphi/2}\cos(\theta/2) \\ e^{\mathrm{i}\varphi/2}\sin(\theta/2)\end{pmatrix}\left(e^{\mathrm{i}\varphi/2}\cos(\theta/2), e^{-\mathrm{i}\varphi/2}\sin(\theta/2)\right) \\ &= \begin{pmatrix} \cos^2(\theta/2) & e^{-\mathrm{i}\varphi}\frac{\sin\theta}{2} \\ e^{\mathrm{i}\varphi}\frac{\sin\theta}{2} & \sin^2(\theta/2)\end{pmatrix},\end{aligned} \tag{2.32}$$

$$\begin{aligned}\psi_-\psi_-^\dagger &= \begin{pmatrix} -e^{-\mathrm{i}\varphi/2}\sin(\theta/2) \\ e^{\mathrm{i}\varphi/2}\cos(\theta/2)\end{pmatrix}\left(-e^{\mathrm{i}\varphi/2}\sin(\theta/2), e^{-\mathrm{i}\varphi/2}\cos(\theta/2)\right) \\ &= \begin{pmatrix} \sin^2(\theta/2) & -e^{-\mathrm{i}\varphi}\frac{\sin\theta}{2} \\ -e^{\mathrm{i}\varphi}\frac{\sin\theta}{2} & \cos^2(\theta/2)\end{pmatrix}.\end{aligned} \tag{2.33}$$

Hence

$$e^{\mathrm{i}\mathbb{O}} = e^{\mathrm{i}a_0}\begin{pmatrix} e^{\mathrm{i}a}\cos^2(\theta/2) + e^{-\mathrm{i}a}\sin^2(\theta/2) & (e^{\mathrm{i}a} - e^{-\mathrm{i}a})e^{-\mathrm{i}\varphi}\frac{\sin\theta}{2} \\ (e^{\mathrm{i}a} - e^{-\mathrm{i}a})e^{\mathrm{i}\varphi}\frac{\sin\theta}{2} & e^{\mathrm{i}a}\sin^2(\theta/2) + e^{-\mathrm{i}a}\cos^2(\theta/2)\end{pmatrix}. \tag{2.34}$$

The (1, 1) matrix element is equivalent to

$$e^{\mathrm{i}a}\cos^2(\theta/2) + e^{-\mathrm{i}a}\sin^2(\theta/2) = \cos a + \mathrm{i}\sin a\cos\theta = \cos a + \mathrm{i}\frac{\sin a}{a}a_3, \tag{2.35}$$

whereas the (2, 2) matrix element is the complex conjugate of the (1, 1) matrix element. For the (2, 1) matrix element we can write

$$(e^{\mathrm{i}a} - e^{-\mathrm{i}a})e^{\mathrm{i}\varphi}\frac{\sin\theta}{2} = \mathrm{i}\sin a\,(\cos\varphi\sin\theta + \mathrm{i}\sin\varphi\sin\theta) = \mathrm{i}\frac{\sin a}{a}(a_1 + \mathrm{i}a_2), \tag{2.36}$$

and similarly for the (1, 2) matrix element we find

$$(e^{\mathrm{i}a} - e^{-\mathrm{i}a})e^{-\mathrm{i}\varphi}\frac{\sin\theta}{2} = \mathrm{i}\frac{\sin a}{a}(a_1 - \mathrm{i}a_2). \tag{2.37}$$

By substituting these results into Eq. (2.34), we arrive at the following important result

$$\boxed{e^{\mathrm{i}\mathbb{O}} = e^{\mathrm{i}a_0}\begin{pmatrix} \cos a + \mathrm{i}\frac{\sin a}{a}a_3 & \mathrm{i}\frac{\sin a}{a}(a_1 - \mathrm{i}a_2) \\ \mathrm{i}\frac{\sin a}{a}(a_1 + \mathrm{i}a_2) & \cos a - \mathrm{i}\frac{\sin a}{a}a_3 \end{pmatrix} = e^{\mathrm{i}a_0}\left(\cos a\,\mathbb{1} + \mathrm{i}\frac{\sin a}{a}\boldsymbol{a}\cdot\boldsymbol{\sigma}\right)} \tag{2.38}$$

We could have obtained the same result using the Taylor series expansion of $e^{i\mathbb{O}}$. We have

$$e^{\mathrm{i}\mathbb{O}} = e^{\mathrm{i}(a_0\mathbb{1} + a\mathbf{n}\cdot\boldsymbol{\sigma})} = e^{\mathrm{i}a_0}e^{\mathrm{i}a\mathbf{n}\cdot\boldsymbol{\sigma}} = e^{\mathrm{i}a_0}\sum_{n=0}^{\infty}\frac{(\mathrm{i}a)^n}{n!}(\mathbf{n}\cdot\boldsymbol{\sigma})^n \tag{2.39}$$

The product of two Pauli matrices is given by

$$\boxed{\sigma_i\sigma_j = \delta_{ij}\mathbb{1} + \mathrm{i}\sum_k \varepsilon_{ijk}\sigma_k} \tag{2.40}$$

and hence

$$(\mathbf{n}\cdot\boldsymbol{\sigma})^2 = \sum_{ij=1}^{3}\frac{a_i a_j}{a^2}\sigma_i\sigma_j = \mathbb{1}. \tag{2.41}$$

Here, we have taken into account that the product $a_i a_j$ is symmetric under the exchange $i \leftrightarrow j$, while the Levi-Civita tensor is antisymmetric, as seen in Appendix B. We then split the Taylor expansion into a sum over even $n = 2p$ and odd $n = 2p + 1$ terms

$$\sum_{n=0}^{\infty}\frac{(\mathrm{i}a)^n}{n!}(\mathbf{n}\cdot\boldsymbol{\sigma})^n = \sum_{p=0}^{\infty}\frac{(\mathrm{i}a)^{2p}}{2p!}\mathbb{1} + \sum_{p=0}^{\infty}\frac{(\mathrm{i}a)^{2p+1}}{(2p+1)!}(\mathbf{n}\cdot\boldsymbol{\sigma}). \tag{2.42}$$

Since $(\mathrm{i}a)^{2p} = \mathrm{i}^{2p}a^{2p} = (-1)^p a^{2p}$ and $(\mathrm{i}a)^{2p+1} = \mathrm{i}^{2p+1}a^{2p+1} = \mathrm{i}\mathrm{i}^{2p}a^{2p+1} = \mathrm{i}(-1)^p a^{2p+1}$, we recognize the Taylor series expansions of the cosine and sine functions. Keeping in mind that $\mathbf{n} = \boldsymbol{a}/a$, we find

$$\sum_{n=0}^{\infty}\frac{(\mathrm{i}a)^n}{n!}(\mathbf{n}\cdot\boldsymbol{\sigma})^n = \cos a\,\mathbb{1} + \mathrm{i}\frac{\sin a}{a}\boldsymbol{a}\cdot\boldsymbol{\sigma} \tag{2.43}$$

By substituting this result into Eq. (2.39), we obtain exactly Eq. (2.38).

2.3 Exercises

1. Consider a two-level quantum system with the Hamiltonian operator $\hat{H}$ and eigenkets $|1\rangle$ and $|2\rangle$ with energies $\hbar\omega$ and $2\hbar\omega$, respectively (i.e., $\hat{H}|n\rangle = n\hbar\omega|n\rangle$ for $n = 1, 2$). Let's consider the operator $\hat{A}$ such that

$$\hat{A}|1\rangle = 3|1\rangle + 4\mathrm{i}|2\rangle, \qquad \hat{A}|2\rangle = -4\mathrm{i}|1\rangle - 3|2\rangle$$

i. Determine the eigenvalues a_1 and a_2 of $\hat{A}$.
ii. If at time zero a measurement of $\hat{A}$ yields the value a_1, what is the probability of measuring a_1 at time t? What about the probability of measuring a_2? And what is the sum of these two probabilities?
Solution *i. The operator $\hat{A}$ has an eigenvalues $a_1 = 5$ and $a_2 = -5$ with a normalized eigenvectors*

$$|\psi_1\rangle = \frac{1}{\sqrt{5}}\left(-2\mathrm{i}|1\rangle + |2\rangle\right) \quad , \quad |\psi_2\rangle = \frac{2}{\sqrt{5}}\left(\frac{\mathrm{i}}{2}|1\rangle + |2\rangle\right).$$

ii. At time zero, the system collapses to $|\psi_1\rangle$, and thus, the state at time t is $|\psi(t)\rangle = \frac{1}{\sqrt{5}}\left(-2\mathrm{i}|1\rangle + |2\rangle e^{-\mathrm{i}\omega t}\right)$. The probability of measuring a_1 at time t is therefore

$$P_1(t) = |\langle\psi_1|\psi(t)\rangle|^2 = \frac{1}{25}\left[17 + 8\cos(\omega t)\right],$$

while the probability of measuring a_2 is

$$P_2(t) = |\langle\psi_2|\psi(t)\rangle|^2 = \frac{8}{25}\left[1 - \cos(\omega t)\right].$$

The sum $P_1(t) + P_2(t)$ correctly equals 1.

2. A two-level system is described by a Hamiltonian represented by the matrix

$$\mathbb{H} = \begin{pmatrix} -\epsilon & 0 \\ 0 & \epsilon \end{pmatrix},$$

with $\epsilon > 0$, and it is in the ground energy state.
i. What is the mean (average) energy?
At a certain instant, an observable Z is measured, represented by the matrix $\mathbb{Z} = \begin{pmatrix} 0 & z \\ z^* & 0 \end{pmatrix}$, with z being a complex number, and the result is found to be $|z|$.
ii. After this measurement, what is the probability of measuring energy $-\epsilon$?
iii. And what is the probability of measuring energy ϵ?
iv. And what is the mean (average) energy?

iv. Determine the change in the mean energy value due to the measurement of the observable Z.

Solution *The eigenvectors of* $\mathbb{H}$ *are* $\begin{pmatrix}1\\0\end{pmatrix}$ *with eigenvalue* $-\epsilon$ *and* $\begin{pmatrix}0\\1\end{pmatrix}$ *with eigenvalue* ϵ*. The eigenvectors of* $\mathbb{Z}$ *are* $\frac{1}{\sqrt{2}}\begin{pmatrix}z/|z|\\1\end{pmatrix}$ *with eigenvalue* $|z|$ *and* $\frac{1}{\sqrt{2}}\begin{pmatrix}-z^*/|z|\\1\end{pmatrix}$ *with eigenvalue* $-|z|$*. Therefore, the probability of measuring* ϵ *or* $-\epsilon$ *after measuring* Z *is 1/2, and it is independent of time. The mean energy is zero, and since it was equal to* $-\epsilon$ *before the measurement of* Z*, we conclude that its change is equal to* ϵ*.*

3. A two-level system is described by the following time-dependent Hamiltonian

$$\mathbb{H}(t) = \begin{cases} -\alpha\hbar\sigma_3 & t < T \\ +\beta\hbar\sigma_3 & t > T \end{cases} .$$

If at time zero, a measurement of σ_1 yields the value 1 with certainty, what must be the value of β so that a measurement of σ_2 at time $t = 2T$ yields -1 with certainty?

Solution *At time zero the wave function of the particle is* $\psi(0) = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}$*. For times* $t > T$ *we have*

$$\psi(t) = \frac{e^{-\mathrm{i}\alpha T+\mathrm{i}\beta(t-T)}}{\sqrt{2}}\begin{pmatrix}e^{2\mathrm{i}\alpha T-2\mathrm{i}\beta(t-T)}\\1\end{pmatrix}$$

So that at time $t = 2T$ *we have probability 1 of measuring* -1 *along the y axis it must be* $\psi(2T) = \frac{e^{\mathrm{i}\theta}}{\sqrt{2}}\begin{pmatrix}\mathrm{i}\\1\end{pmatrix}$ *with* θ *an arbitrary phase. It is then immediate to obtain that* $\beta = \alpha + \frac{\pi}{4T}$*.*

4. Consider a quantum two-level system. In a certain basis, the representation of three operators $\hat{A}$, $\hat{B}$, and $\hat{C}$ is as follows:

$$\mathbb{A} = \begin{pmatrix}1 & 2\sqrt{2}\\ 2\sqrt{2} & 3\end{pmatrix} \quad , \quad \mathbb{B} = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} \quad , \quad \mathbb{C} = \begin{pmatrix}0 & -\mathrm{i}\\ \mathrm{i} & 0\end{pmatrix}$$

Knowing that:
(1) The probability of measuring the observable A and obtaining the value -1 is $\frac{1}{2}$
(2) The probability of measuring the observable B and obtaining the value 1 is $\frac{5}{6}$
(3) The average value of the observable C is $\frac{1}{\sqrt{2}}$.
Determine the two-component vector representing the state of the system in the given basis.

Solution *The matrix* $\mathbb{A}$ *has eigenvalues* $a_1 = 5$ *and* $a_2 = -1$*. The corresponding normalized eigenvectors are:*

$$\mathbf{a}_1 = \frac{1}{\sqrt{3}}\begin{pmatrix} 1 \\ \sqrt{2} \end{pmatrix} \quad , \quad \mathbf{a}_2 = \frac{1}{\sqrt{3}}\begin{pmatrix} \sqrt{2} \\ -1 \end{pmatrix}$$

From point (1), we deduce that the vector describing the system must have the following structure:

$$\mathbf{v} = \frac{1}{\sqrt{2}}\left(\mathbf{a}_1 + e^{\mathrm{i}\phi}\mathbf{a}_2\right) = \frac{1}{\sqrt{6}}\begin{pmatrix} 1+\sqrt{2}e^{\mathrm{i}\phi} \\ \sqrt{2}-e^{\mathrm{i}\phi} \end{pmatrix}$$

where the phase ϕ *needs to be determined using points (2) and (3). From point (2), we have*

$$P(B=-1) = |(1,0)\cdot\mathbf{v}|^2 = \frac{1}{6}\left|(1,0)\cdot\begin{pmatrix} 1+\sqrt{2}e^{\mathrm{i}\phi} \\ \sqrt{2}-e^{\mathrm{i}\phi} \end{pmatrix}\right|^2 = \frac{1}{2}+\frac{\sqrt{2}}{3}\cos\phi = \frac{5}{6}$$

from which it follows that $\cos\phi = \frac{1}{\sqrt{2}}$*, and therefore,* $\phi = \pm\frac{\pi}{4}$*. To determine the sign of* ϕ *we use the last point. The expectation value of the observable C is given by:*

$$\mathbf{v}^\dagger\mathbb{C}\mathbf{v} = \frac{1}{6}(1+\sqrt{2}e^{-\mathrm{i}\phi}, \sqrt{2}-e^{-\mathrm{i}\phi})\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}\begin{pmatrix} 1+\sqrt{2}e^{\mathrm{i}\phi} \\ \sqrt{2}-e^{\mathrm{i}\phi} \end{pmatrix} = -\sin\phi = \frac{1}{\sqrt{2}}.$$

We conclude that $\phi = -\frac{\pi}{4}$.

5. Consider a quantum system with three levels. In a certain basis, the representation of three operators $\hat{H}$, $\hat{A}$, $\hat{B}$ is as follows:

$$\mathbb{H} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad , \quad \mathbb{A} = \begin{pmatrix} 0 & -\mathrm{i} & 0 \\ \mathrm{i} & 0 & -\mathrm{i} \\ 0 & \mathrm{i} & 0 \end{pmatrix} \quad , \quad \mathbb{B} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \tag{2.44}$$

Determine the three-component vector representing the state of the system, knowing that:
(1) The system is in an eigenstate of the Hamiltonian operator $\hat{H}$ with energy -1,
(2) The expectation value of the operator $\hat{A}$ in this state is $-\frac{2}{3}$,
(3) The expectation value of the operator $\hat{B}$ in this state is zero.

Solution *The matrix* $\mathbb{H}$ *is block diagonal, and its eigenvalues are* $\epsilon_1 = 1$ *and* $\epsilon_2 = -1$ *from the upper* 2×2 *block, and* $\epsilon_3 = -1 = \epsilon_2$ *from the lower* 1×1 *block. Therefore, the eigenvalue* -1 *has a degeneracy of two. The respective eigenvectors are:*

$$\vec{\psi}_1 = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix} \quad , \quad \vec{\psi}_2 = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix} \quad , \quad \vec{\psi}_3 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

From information (1), we know that the state of the system $\vec{\psi}$ *can be written as a generic linear combination (normalized) of eigenvectors with eigenvalue –1, and therefore as* $\vec{\psi} = a\vec{\psi}_2 + be^{\mathrm{i}\phi}\vec{\psi}_3$, *with* a, b, *and* ϕ *as real constants to be determined.*
From information (2) we know that

$$\left(\frac{a}{\sqrt{2}}, -\frac{a}{\sqrt{2}}, be^{-\mathrm{i}\phi}\right)\begin{pmatrix} 0 & -\mathrm{i} & 0 \\ \mathrm{i} & 0 & -\mathrm{i} \\ 0 & \mathrm{i} & 0 \end{pmatrix}\begin{pmatrix} \frac{a}{\sqrt{2}} \\ -\frac{a}{\sqrt{2}} \\ be^{\mathrm{i}\phi} \end{pmatrix} = -\sqrt{2}ab\sin\phi = -\frac{2}{3}.$$

From information (3) we further know that

$$\left(\frac{a}{\sqrt{2}}, -\frac{a}{\sqrt{2}}, be^{-\mathrm{i}\phi}\right)\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} \frac{a}{\sqrt{2}} \\ -\frac{a}{\sqrt{2}} \\ be^{\mathrm{i}\phi} \end{pmatrix} = \frac{a^2}{2} - b^2 = 0.$$

Using this last relationship together with the normalization condition, we immediately find $a = \sqrt{\frac{2}{3}}$ *and* $b = \frac{1}{\sqrt{3}}$. *Substituting these values into the equation for the average of* $\hat{A}$, *we obtain* $\sin\phi = 1$, *and thus* $\phi = \frac{\pi}{2}$.
We conclude that the sought state is

$$\vec{\psi} = \frac{1}{\sqrt{3}}\begin{pmatrix} 1 \\ -1 \\ \mathrm{i} \end{pmatrix}$$

6. A three-level quantum system is at time $t = 0$ in the state $|\psi\rangle$, which, in a certain basis, is represented by the vector $\boldsymbol{\psi} = \frac{1}{\sqrt{2}}\begin{pmatrix} -1 \\ 0 \\ 1 \end{pmatrix}$. The system begins to evolve according to the Schrödinger equation with a Hamiltonian $\hat{H}(t)$ that, in the same basis, is represented by the matrix

$$\mathbb{H}(t) = E_0\left[\theta(t)\mathbb{A} - \theta(t-T)\sin(\frac{\pi}{2}\mathbb{A})\right] \quad \text{with} \quad \mathbb{A} = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & -\mathrm{i} & 0 \\ \mathrm{i} & 0 & -\mathrm{i} \\ 0 & \mathrm{i} & 0 \end{pmatrix}.$$

Assuming $T > 0$
i. Determine the eigenvectors and eigenvalues of $\mathbb{H}(t)$ for times $0 < t < T$ and for times $T < t$.
ii. Determine the evolved vector $\boldsymbol{\psi}(t)$ for all times $t > 0$.
iii. Calculate the average energy value $\boldsymbol{\psi}^\dagger(t)\mathbb{H}(t)\boldsymbol{\psi}(t)$ for all times $t > 0$.
iv. Determine how the probability $P(t)$ that a measurement of energy yields a null result evolves over time.

Solution *i. Since* $[\mathbb{H}(t), \mathbb{A}] = 0$ *at all times, the eigenvectors of* $\mathbb{A}$ *are also eigenvectors of* $\mathbb{H}(t)$. *The diagonalization of* $\mathbb{A}$ *immediately provides the eigenvalues* $\lambda_1 = -1$, $\lambda_2 = 0$, $\lambda_3 = 1$, *and their corresponding eigenvectors*

$$\mathbf{v}_1 = \frac{1}{2}\begin{pmatrix} -1 \\ \mathrm{i}\sqrt{2} \\ 1 \end{pmatrix} \quad , \quad \mathbf{v}_2 = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix} \quad , \quad \mathbf{v}_3 = \frac{1}{2}\begin{pmatrix} -1 \\ -\mathrm{i}\sqrt{2} \\ 1 \end{pmatrix}.$$

Therefore, the eigenvalues of $\mathbb{H}(t)$ are

$$0 < t < T \rightarrow \begin{cases} E_1 = E_0\lambda_1 = -E_0 \\ E_2 = E_0\lambda_2 = 0 \\ E_3 = E_0\lambda_3 = E_0 \end{cases} \qquad T < t \rightarrow \begin{cases} E_1 = E_0[\lambda_1 - \sin(\frac{\pi}{2}\lambda_1)] = 0 \\ E_2 = E_0[\lambda_2 - \sin(\frac{\pi}{2}\lambda_2)] = 0 \\ E_3 = E_0[\lambda_3 - \sin(\frac{\pi}{2}\lambda_3)] = 0 \end{cases}$$

ii. To determine the temporal evolution of the system, it is necessary to express the initial state ψ *as a linear combination of* $\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_3$. *To do this, it is straightforward to verify that*

$$\psi = \frac{\mathbf{v}_1 + \mathbf{v}_3}{\sqrt{2}},$$

and therefore the temporal evolution yields

$$\psi(t) = \frac{1}{\sqrt{2}} \times \begin{cases} \mathbf{v}_1 e^{\mathrm{i}E_0 t/\hbar} + \mathbf{v}_3 e^{-\mathrm{i}E_0 t/\hbar} & 0 < t < T \\ \mathbf{v}_1 e^{\mathrm{i}E_0 T/\hbar} + \mathbf{v}_3 e^{-\mathrm{i}E_0 T/\hbar} & t > T \end{cases}$$

iii. The average value of the energy is

$$E(t) = \psi^\dagger(t)\mathbb{H}(t)\psi(t) = \frac{1}{2}(E_1 + E_3) = 0$$

for all times.

iv. To determine the probability $P(t)$ *that a measurement of energy yields a null result, one must calculate the sum of the squared moduli of the scalar products between* $\psi(t)$ *and all the eigenvectors of* $\mathbb{H}(t)$ *that at time t have an eigenvalue of zero*

$$P(t) = \begin{cases} |\mathbf{v}_2^\dagger\psi(t)|^2 = 0 & 0 < t < T \\ \\ |\mathbf{v}_1^\dagger\psi(t)|^2 + |\mathbf{v}_2^\dagger\psi(t)|^2 + |\mathbf{v}_3^\dagger\psi(t)|^2 = 1 & t > T \end{cases}$$

7. The spin operators are represented as $\mathbb{S}_x = \frac{\hbar}{2}\sigma_x$, $\mathbb{S}_y = \frac{\hbar}{2}\sigma_y$, and $\mathbb{S}_z = \frac{\hbar}{2}\sigma_z$, where σ_i are the Pauli matrices. Consider a state described at time $t = 0$ by the vector $\psi(0) = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$. If the temporal evolution is governed by the Hamiltonian

$$\mathbb{H} = 2b \begin{cases} \mathbb{S}_y & t < \frac{3\pi}{4b} \\ \mathbb{S}_z & t > \frac{3\pi}{4b} \end{cases}$$

calculate the probability that a measurement of $\hat{S}_z$ yields the value $\hbar/2$ for a generic time $t > 0$ (consider both the cases $t < \frac{3\pi}{4b}$ and $t > \frac{3\pi}{4b}$).

Solution *For* $t < \frac{3\pi}{4b}$*, the vector at time t is given by* $\psi(t) = e^{-\mathrm{i}2b\mathbb{S}_y t/\hbar}\vec{\psi}(0) = e^{\mathrm{i}b\sigma_y t}\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}$. *Taking into account that the normalized eigenvectors of* σ_y are $\frac{1}{\sqrt{2}}\begin{pmatrix}1\\\mathrm{i}\end{pmatrix}$ *and* $\frac{1}{\sqrt{2}}\begin{pmatrix}1\\iu\end{pmatrix}$ *with eigenvalues* 1 *and* -1 *respectively, we have*

$$e^{-\mathrm{i}b\sigma_y t} = e^{-\mathrm{i}bt}\frac{1}{2}\begin{pmatrix}1\\\mathrm{i}\end{pmatrix}(1, -\mathrm{i}) + e^{\mathrm{i}bt}\frac{1}{2}\begin{pmatrix}1\\iu\end{pmatrix}(1, \mathrm{i}).$$

Using this result, it is easy to obtain $\psi(t) = \frac{1}{\sqrt{2}}\begin{pmatrix}\cos bt - \sin bt\\ \cos bt + \sin bt\end{pmatrix}$*, and therefore, the probability that at time* $t < \frac{3\pi}{4b}$ *a measurement of spin along the z axis yields* $\hbar/2$ *is*

$$P\left(t < \frac{3\pi}{4b}\right) = |(1, 0) \cdot \psi(t)|^2 = \frac{1}{2}(1 - \sin 2bt)$$

For $t > \frac{3\pi}{4b}$*, the Hamiltonian commutes with the observable* $\hat{S}_z$*, and therefore, the probability no longer depends on time. We then have*

$$P\left(t > \frac{3\pi}{4b}\right) = P\left(\frac{3\pi}{4b}\right) = 1$$

8. In a Hilbert space of dimension 5 the representation of the Hamiltonian in a certain basis is given by

$$\mathbb{H} = E_0\mathbb{X}, \qquad \mathbb{X} = \frac{1}{5}\begin{pmatrix}1&1&1&1&1\\1&1&1&1&1\\1&1&1&1&1\\1&1&1&1&1\\1&1&1&1&1\end{pmatrix}$$

with $E_0 \neq 0$. In the same basis the state of the system at time $t = 0$ is described from the vector $\mathbf{\Psi}_0 = (1, 0, 0, 0, 0)^T$
i. Determine whether the vector $\mathbf{\Phi} = \frac{1}{\sqrt{5}}(1, 1, 1, 1, 1)^T$ is an eigenvector of $\mathbb{H}$ and if so, determine its eigenvalue.
ii. Calculate the vector $\mathbf{\Psi}(t) = \exp[-\mathrm{i}\mathbb{H}t/\hbar]\mathbf{\Psi}_0$ that describes the state of the system at time $t > 0$ (Hint: calculate $\mathbb{X}^2$)

iii. Use the result of the previous step to calculate the probability of measuring energy $E = 0$ at time $t > 0$

Solution *It is easy to verify that* $\mathbf{\Phi} = \frac{1}{\sqrt{5}}(1, 1, 1, 1, 1)^T$ *is an eigenvector of* $\mathbb{H}$ *with eigenvalue* E_0. *Following the hint we find* $\mathbb{X}^2 = \mathbb{X}$ *e so* $\mathbb{X}^n = \mathbb{X}$ *for every positive integer n. It follows that*

$$\begin{aligned}\exp[-\mathrm{i}\mathbb{H}t/\hbar] &= 1 + \frac{1}{1!}\left(\frac{-\mathrm{i}E_0 t}{\hbar}\right)\mathbb{X} + \frac{1}{2!}\left(\frac{-\mathrm{i}E_0 t}{\hbar}\right)^2\mathbb{X} + \frac{1}{3!}\left(\frac{-\mathrm{i}E_0 t}{\hbar}\right)^3\mathbb{X} + \cdots\\ &= \left[(1 - \mathbb{X}) + e^{-\mathrm{i}E_0 t/\hbar}\mathbb{X}\right]\end{aligned}$$

Therefore the state at time $t > 0$ *is described by the vector*

$$\mathbf{\Psi}(t) = \left[(1 - \mathbb{X}) + e^{-\mathrm{i}E_0 t/\hbar}\mathbb{X}\right]\begin{pmatrix}1\\0\\0\\0\\0\end{pmatrix} = \frac{1}{5}\begin{pmatrix}4\\-1\\-1\\-1\\-1\end{pmatrix} + \frac{e^{-\mathrm{i}E_0 t/\hbar}}{5}\begin{pmatrix}1\\1\\1\\1\\1\end{pmatrix}$$

The Hamiltonian all has equal rows, so we have four zero eigenvalues and one non-zero eigenvalue. The latter must necessarily be E_0 *whose eigenvector we have established previously to be* $\mathbf{\Phi}$. *It follows that the probability of measuring* E_0 *at time t is given by*

$$P(E_0, t) = \left|\mathbf{\Phi}^T \cdot \mathbf{\Psi}(t)\right|^2 = \frac{1}{5}$$

Therefore the probability of measuring energy $E = 0$ *is equal to* 4/5.

9. A two-level quantum system is described by a Hamiltonian $\hat{H}$ that, in a certain orthonormal basis, is represented by the matrix $\mathbb{H}$. Determine the matrix $\mathbb{H}$ given that:

(1) The sum of its eigenvalues is zero, and the energy of the ground state is greater than $-2E_0$, where $E_0 > 0$;

(2) $\mathbb{H}$ commutes with the Pauli matrix σ_y;

(3) The average of $\mathbb{H}$ over the state described by the vector $\frac{1}{\sqrt{2}}\begin{pmatrix}1\\\mathrm{i}\end{pmatrix}$ is positive.

(4) If at time $t = 0$ the system is in the state described by the vector $\mathbf{v}$, following the temporal evolution, the state returns to itself at time $t = 3\hbar/E_0$.

Solution *The most general matrix representation we can write is a combination of the* 2×2 *identity matrix and the three Pauli matrices. From information (1), we deduce that the coefficient of the identity matrix must be zero. From information (2), it must be the case that* $\mathbb{H} = \gamma\sigma_y$ with γ *real. The eigenvalues of* $\mathbb{H}$ are then $\epsilon_\pm = \pm\gamma$, *with corresponding eigenvectors* $\psi_+ = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\\mathrm{i}\end{pmatrix}$ *and* $\psi_- = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\iu\end{pmatrix}$. *From information (3), we deduce that* $\gamma > 0$.

Let us now use information (4). The vector $\mathbf{v}$ *can be written as* $\mathbf{v} = \alpha_+ \boldsymbol{\psi}_+ + \alpha_- \boldsymbol{\psi}_-$. *Therefore, the temporal evolution of the state vector is*

$$\begin{aligned} \mathbf{v}(t) &= \alpha_+ e^{-\mathrm{i}\epsilon_+ t/\hbar} \boldsymbol{\psi}_+ + \alpha_- e^{-\mathrm{i}\epsilon_- t/\hbar} \boldsymbol{\psi}_- \\ &= \alpha_+ e^{-\mathrm{i}\gamma t/\hbar} \boldsymbol{\psi}_+ + \alpha_- e^{\mathrm{i}\gamma t/\hbar} \boldsymbol{\psi}_- \\ &= e^{-\mathrm{i}\gamma t/\hbar} \left[\alpha_+ \boldsymbol{\psi}_+ + \alpha_- e^{2\mathrm{i}\gamma t/\hbar} \boldsymbol{\psi}_- \right]. \end{aligned} \tag{2.45}$$

Therefore, at time $t = 3\hbar/E_0$, *the vector* $\mathbf{v}(3\hbar/E_0)$ *is (up to an irrelevant phase factor) identical to* $\mathbf{v}$ *if* $6\gamma = 2n\pi E_0$, *where n is a positive integer. Remembering that the energy of the ground state must be greater than* $-2E_0$, *it follows that* $\gamma = \pi E_0/3$. *In conclusion,* $\mathbb{H} = \frac{\pi E_0}{3}\sigma_y$.

10. In a certain orthonormal basis the Hamiltonian $\mathbb{H}$ and the observables $\mathbb{A}$ and $\mathbb{B}$ are described by matrices 3 × 3

$$\mathbb{H} = \begin{pmatrix} 0 & 0 & -\mathrm{i} \\ 0 & 1 & 0 \\ \mathrm{i} & 0 & 0 \end{pmatrix} \quad , \quad \mathbb{A} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 3 \end{pmatrix} \quad , \quad \mathbb{B} = \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix}$$

Determine the column vector $\boldsymbol{\psi} = (\psi_1, \psi_2, \psi_3)^T$ normalized to 1 knowing that
i. An energy measurement gives result 1
ii. The probability that a measure of $\mathbb{A}$ provides value 2 is equal to 1/3
iii. The average value of the observable $\mathbb{B}$ is equal to 1
iv. The real part of the ratio ψ_3/ψ_2 is positive, i.e, $\Re[\psi_3/\psi_2] > 0$
Solution *The eigenvectors of* $\mathbb{H}$ *with eigenvalue* 1 *are* $\mathbf{v} = (0, 1, 0)^T$ *and* $\mathbf{w} = \frac{1}{\sqrt{2}}(-\mathrm{i}, 0, 1)^T$. *So from the first information we can write* $\boldsymbol{\psi} = \cos\theta\, \mathbf{v} + e^{\mathrm{i}\phi} \sin\theta\, \mathbf{w}$.
From the second piece of information we have that $|(0, 1, 0) \cdot \boldsymbol{\psi}|^2 = \cos^2\theta = 1/3$ *and therefore* $\sin^2\theta = 2/3$. *We can therefore write that* $\boldsymbol{\psi} = \frac{1}{\sqrt{3}}(-\mathrm{i}e^{\mathrm{i}\phi}, 1, e^{\mathrm{i}\phi})^T$.
From the third piece of information we know that $\boldsymbol{\psi}^\dagger \mathbb{B}\, \boldsymbol{\psi} = 1$. *Turns out* $\boldsymbol{\psi}^\dagger \mathbb{B}\, \boldsymbol{\psi} = \frac{1}{3}|1 + (1 - \mathrm{i})e^{\mathrm{i}\phi}|^2 = 1 + \frac{2}{3}(\cos\phi + \sin\phi)$ *from which* $\cos\phi = -\sin\phi$ *follows. Therefore* $e^{\mathrm{i}\phi} = \pm e^{-\mathrm{i}\pi/4}$ *and therefore* $\boldsymbol{\psi} = \frac{1}{\sqrt{3}}(\mp\mathrm{i}e^{-\mathrm{i}\pi/4}, 1, \pm e^{-\mathrm{i}\pi/4})^T$.
From the last information we have that $\Re[\psi_3/\psi_2] = \pm\cos(\pi/4) > 0$. *Therefore we must choose the upper sign. In conclusion* $\boldsymbol{\psi} = \frac{1}{\sqrt{3}}(-\mathrm{i}e^{-\mathrm{i}\pi/4}, 1, e^{-\mathrm{i}\pi/4})^T$.

11. In a certain basis the Hamiltonian $\hat{H}$ of a two-quantum system levels is represented by the matrix $\mathbb{H}$. Determine $\mathbb{H}$ knowing that:
(1) The sum of its eigenvalues is 3;
(2) The average of $\mathbb{H}$ on state $\boldsymbol{\psi} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ is 2;
(3) The energy of the ground state of $\mathbb{H}$ is 0;

(4) If at time $t = 0$ the system is in the state ψ, al time $t = \hbar\pi/3$ the state of the system $\psi(t)$ is orthogonal to the state $\boldsymbol{\xi} = \frac{1}{3}\begin{pmatrix} 2\sqrt{2} \\ 1 \end{pmatrix}$

Solution *The searched matrix can be written in complete generality as*

$$\mathbb{H} = \begin{pmatrix} a & ce^{\mathrm{i}\phi} \\ ce^{-\mathrm{i}\phi} & b \end{pmatrix}$$

with a, b, c *real,* $c \geq 0$ *and* $0 \leq \phi \leq 2\pi$. *From information (1) we know that* $a + b = 3$, *while from information (2) we immediately find that* $a = 2$, *from which* $b = 1$ *follows. The eigenvalues of the matrix* $\mathbb{H} = \begin{pmatrix} 2 & ce^{\mathrm{i}\phi} \\ ce^{-\mathrm{i}\phi} & 1 \end{pmatrix}$ *are* $\lambda_\pm = \frac{1}{2}(3 \pm \sqrt{1 + 4c^2})$. *Using information (3) it follows that* $c = \sqrt{2}$. *By imposing this value the eigenvalues of* $\mathbb{H}$ *are therefore* $\lambda_- = 0$ *and* $\lambda_+ = 3$, *with respective eigenvectors*

$$\boldsymbol{\lambda}_- = \sqrt{\frac{2}{3}}\begin{pmatrix} e^{\mathrm{i}\phi}/\sqrt{2} \\ -1 \end{pmatrix} \qquad \boldsymbol{\lambda}_+ = \frac{1}{\sqrt{3}}\begin{pmatrix} e^{\mathrm{i}\phi}\sqrt{2} \\ 1 \end{pmatrix}$$

Using these expressions the temporal evolution of ψ *is*

$$\psi(t) = \frac{e^{-\mathrm{i}\phi}}{\sqrt{3}}\boldsymbol{\lambda}_- + \sqrt{\frac{2}{3}}e^{-\mathrm{i}\phi - \mathrm{i}3t/\hbar}\boldsymbol{\lambda}_+$$

At time $t = \hbar\pi/3$ *this state is equal to*

$$\psi(\hbar\pi/3) = -\frac{1}{3}\begin{pmatrix} 1 \\ 2\sqrt{2}e^{\mathrm{i}\phi} \end{pmatrix}$$

which is orthogonal to the state $\boldsymbol{\xi}$ *for* $\phi = \pi$.

The searched matrix is therefore $\mathbb{H} = \begin{pmatrix} 2 & -\sqrt{2} \\ -\sqrt{2} & 1 \end{pmatrix}$.

12. In a certain basis the Hamiltonian $\hat{H}$ of a two-level quantum system and an observable $\hat{A}$ are represented by the matrices

$$\mathbb{H} = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \quad , \quad \mathbb{A} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

In the same basis, determine the column vector $\boldsymbol{\Psi}$ representative of the state of the system knowing that

(1) $\boldsymbol{\Psi}^\dagger[\mathbb{H}, \mathbb{A}]\boldsymbol{\Psi} = 0$;

(2) the probability that an energy measurement provides value -1 is $\frac{1}{2} - \frac{\sqrt{3}}{4}$;

(3) the average value of $\hat{A}$ is $\frac{1}{2}$.

Solution *The searched column vector can be written in complete generalities like*

$$\boldsymbol{\Psi} = \begin{pmatrix} \cos\theta \\ e^{\mathrm{i}\phi}\sin\theta \end{pmatrix}$$

with $0 \le \theta \le \pi/2$ and $0 \le \phi \le 2\pi$. *From information (1) we find*

$$-2\mathrm{i}\boldsymbol{\Psi}^{\dagger}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\boldsymbol{\Psi} = -2\mathrm{i}\cos 2\theta = 0\,,$$

from which we can deduce $\theta = \pi/4$. *Knowing that the eigenvector of* $\mathbb{H}$ *with eigenvalue* -1 *is*

$$\boldsymbol{\phi} = \frac{1}{\sqrt{2}}\begin{pmatrix} \mathrm{i} \\ 1 \end{pmatrix}$$

from information (2) we find that $|\boldsymbol{\phi}^{\dagger}\cdot\boldsymbol{\Psi}|^2 = \frac{1}{2}(1-\sin\phi) = \frac{1}{2} - \frac{\sqrt{3}}{4}$ *from which we can deduce* $\sin\phi = \sqrt{3}/2$ *and therefore* $\phi = \frac{\pi}{3}$ or $\phi = \frac{2}{3}\pi$. *To understand which of the two solutions is acceptable we must use information (3), on the basis of which* $\boldsymbol{\Psi}^{\dagger}\mathbb{A}\boldsymbol{\Psi} = \boldsymbol{\Psi}^{\dagger}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\boldsymbol{\Psi} = \cos\phi = \frac{1}{2}$, *so we are forced to choose* $\phi = \frac{\pi}{3}$. *The searched vector is therefore*

$$\boldsymbol{\Psi} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ e^{\mathrm{i}\pi/3} \end{pmatrix}$$

13. A quantum system with three levels is described by the Hamiltonian

$$\mathbb{H} = E\begin{pmatrix} 3/2 & 0 & \mathrm{i}/2 \\ 0 & 1 & 0 \\ -\mathrm{i}/2 & 0 & 3/2 \end{pmatrix}$$

Find the eigenvalues, their degeneracy, and an orthonormal basis of eigenvectors.
Solution *The Hamiltonian* $\mathbb{H}$ *has eigenvalues* $E_1 = 1$ *with eigenvector* $\boldsymbol{\phi}_1 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$, $E_2 = 1$ *with eigenvector* $\boldsymbol{\phi}_2 = \frac{1}{\sqrt{2}}\begin{pmatrix} -\mathrm{i} \\ 0 \\ 1 \end{pmatrix}$, *and* $E_3 = 2$ *with eigenvector* $\boldsymbol{\phi}_3 = \frac{1}{\sqrt{2}}\begin{pmatrix} \mathrm{i} \\ 0 \\ 1 \end{pmatrix}$.

More Exercises

14. At time $t = 0$ a two-level system is described by vector $\psi_0 = \frac{1}{\sqrt{3}}\begin{pmatrix} \sqrt{2} \\ -1 \end{pmatrix}$. The state evolves over time according to the Schrödinger equation with Hamiltonian

$$\mathbb{H}(t) = \sqrt{2}E \begin{pmatrix} 0 & e^{-\mathrm{i}Et/\hbar} \\ e^{\mathrm{i}Et/\hbar} & 0 \end{pmatrix}$$

i. Calculate the vector $\psi(t)$ that describes the system at time t (Hint: Look for solutions of the form $\psi(t) = \begin{pmatrix} ae^{\mathrm{i}\alpha t} \\ be^{\mathrm{i}\beta t} \end{pmatrix}$ with a, b, α and β to be determined).
ii. Calculate the ground state $\boldsymbol{\xi}(t)$ of $\mathbb{H}(t)$.
iii. Calculate the average value of the observable represented by matrix σ_2.
iv. Calculate the probability of measuring at time t the ground state energy of $\mathbb{H}(t)$.

15. In the basis $\{|R_1\rangle, |R_2\rangle\}$ the Hamiltonian of the molecular ion H_2^+ is described by the matrix

$$\mathbb{H} = \begin{pmatrix} E_0 & V(R) \\ V(R) & E_0 \end{pmatrix}$$

where $E_0 = -13.6$ eV, $R = |R_1 - R_2|$ is the distance between the two nuclei and the function $V(R) = V_0 e^{-\alpha(R-R_{\mathrm{eq}})}$ with $V_0 = 0.2$ eV and R_{eq} is the distance between the two nuclei in their equilibrium position.
i. Calculate the ground state energy of the molecular ion ($R = R_{\mathrm{eq}}$) and the energy of the ground state of the dissociated ion ($R \to \infty$) ed extract the binding energy from their difference.
ii. Write the eigenkets of the Hamiltonian as a linear combination of $|R_1\rangle$ and $|R_2\rangle$ for a generic R.

16. In a Hilbert space of dimension three it is given the orthonormal basis $|1\rangle$, $|2\rangle$ and $|3\rangle$ and two operators $\hat{A}$ and $\hat{B}$ whose action on the bases kets is

$$\begin{aligned} \hat{A}|1\rangle &= 3|1\rangle - \mathrm{i}\sqrt{2}|2\rangle + |3\rangle & \hat{B}|1\rangle &= |1\rangle + \mathrm{i}\sqrt{2}|2\rangle + |3\rangle \\ \hat{A}|2\rangle &= \mathrm{i}\sqrt{2}|1\rangle + 2|2\rangle - \mathrm{i}\sqrt{2}|3\rangle & \hat{B}|2\rangle &= -\mathrm{i}\sqrt{2}|1\rangle + \mathrm{i}\sqrt{2}|3\rangle \\ \hat{A}|3\rangle &= |1\rangle + \mathrm{i}\sqrt{2}|2\rangle + 3|3\rangle & \hat{B}|3\rangle &= |1\rangle - \mathrm{i}\sqrt{2}|2\rangle + |3\rangle \end{aligned}$$

i. Determine the representation of the operators $\hat{A}$ e $\hat{B}$ in the basis $|1\rangle$, $|2\rangle$ and $|3\rangle$.
ii. Write the operators $\hat{A}$ e $\hat{B}$ as $\hat{A} = \sum_{ij=1}^{3} c_{ij}^{A} |i\rangle\langle j|$ and $\hat{B} = \sum_{ij=1}^{3} c_{ij}^{B} |i\rangle\langle j|$ choosing appropriately the coefficients c_{ij}^{A} and c_{ij}^{B}.
iii. Are the operators $\hat{A}$ and $\hat{B}$ Hermitian?
iv. Calculate the commutator $[\hat{A}, \hat{B}]$.
If possible find a common base $|v_1\rangle$, $|v_2\rangle$ e $|v_3\rangle$ of eigenkets of $\hat{A}$ and $\hat{B}$ and write the representation of the operators in this new basis.

Chapter 3
Quantum Particle in One Dimension

In this chapter, we study problems in quantum mechanics for a single particle in one dimension.

3.1 Momentum Operator and Hamiltonian

In Sect. 1.6 we have seen that the scalar product between a position eigenket $|x\rangle$ and a momentum eigenket $|p\rangle$ is given by Eq. (1.128):

$$\langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{\frac{\mathrm{i}px}{\hbar}}. \tag{3.1}$$

The function on the right-hand side of the equation is also called a **plane wave**. It is straightforward to verify that for a plane wave

$$\boxed{-\mathrm{i}\hbar\frac{\partial}{\partial x}\langle x|p\rangle = p\langle x|p\rangle} \tag{3.2}$$

Now, let's consider a general ket $|\Psi\rangle$ describing our particle in one dimension, and learn how to calculate $\langle x|\hat{p}|\Psi\rangle$, where $\hat{p}$ is the momentum operator with eigenkets $|p\rangle$ having eigenvalue p. By inserting the resolution of the identity

$$\begin{aligned}\langle x|\hat{p}|\Psi\rangle &= \int dp\langle x|\hat{p}|p\rangle\langle p|\Psi\rangle = \int dp\; p\langle x|p\rangle\langle p|\Psi\rangle = -\mathrm{i}\hbar\frac{\partial}{\partial x}\int dp\langle x|p\rangle\langle p|\Psi\rangle \\ &= -\mathrm{i}\hbar\frac{\partial}{\partial x}\langle x|\Psi\rangle. \end{aligned} \tag{3.3}$$

The scalar product $\Psi(x) = \langle x|\Psi\rangle$ is the wave function that we have already encountered in Sect. 1.4, whose square modulus provides the probability density of finding the electron at position x.

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The steps just taken can be easily repeated for an arbitrary power of $\hat{p}$. In fact, it is straightforward to verify that $(-i\hbar)^n \frac{d^n}{dx^n}\langle x|p\rangle = p^n\langle x|p\rangle$, and therefore

$$\boxed{\langle x|\hat{p}^n|\Psi\rangle = (-\mathrm{i}\hbar)^n \frac{\partial^n}{\partial x^n}\Psi(x)} \tag{3.4}$$

This means that if we have a function $f(p)$ that can be expanded in a Taylor series as $f(p) = \sum_{n=0}^{\infty} \frac{f^{(n)}(0)}{n!} p^n$ then

$$\boxed{\langle x|f(\hat{p})|\Psi\rangle = f\left(-\mathrm{i}\hbar\frac{\partial}{\partial x}\right)\Psi(x)} \tag{3.5}$$

With these premises, we can tackle many problems in one dimension. If the particle is subject to a potential $V(x)$ that depends only on position, then its Lagrangian is

$$\mathcal{L} = \frac{1}{2}m\dot{x}^2 - V(x). \tag{3.6}$$

The conjugate momentum is then

$$p = \frac{\partial \mathcal{L}}{\partial \dot{x}} = m\dot{x} \tag{3.7}$$

from which we find $\dot{x} = p/m$. This allows us to obtain the Hamiltonian from the Legendre transform

$$H = p\dot{x} - \mathcal{L} = \frac{p^2}{2m} + V(x). \tag{3.8}$$

Therefore, the Schrödinger equation for a particle in one dimension subjected to the potential $V(x)$ is written as follows

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle = \left(\frac{\hat{p}^2}{2m} + V(\hat{x})\right)|\Psi(t)\rangle. \tag{3.9}$$

In Eq. (3.9), the unknown object to determine is the ket $|\Psi(t)\rangle$. To find it, it is often useful to transform the equation into an equation for the wave function $\Psi(x,t) = \langle x|\Psi(t)\rangle$. Clearly, knowing the wave function is equivalent to knowing the ket, as $|\Psi(t)\rangle = \int dx \Psi(x,t)|x\rangle$. Multiplying Eq. (3.9) by the bra $\langle x|$ we obtain

$$\boxed{\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(x,t) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\Psi(x,t)} \tag{3.10}$$

where we use Eq. (3.4) and the fact that $\langle x|V(\hat{x}) = \langle x|V(x)$.

A common way to proceed at this point is to find the eigenfunctions $\psi_{E,k}(x) = \langle x|E,k\rangle$ of the Hamiltonian:

$$\left(\frac{\hat{p}^2}{2m} + V(\hat{x})\right)|E,k\rangle = E|E,k\rangle \qquad \Rightarrow \qquad \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\varphi_{E,k}(x) = E\varphi_{E,k}(x). \tag{3.11}$$

Indeed, the set of kets $|E,k\rangle$ forms a basis, and therefore, we can always expand $|\Psi(t)\rangle$ on this basis. As seen in Sect. 1.7, the solution is given by

$$|\Psi(t)\rangle = \sum_{E,k} c_{E,k}(0)e^{-\mathrm{i}\frac{Et}{\hbar}}|E,k\rangle \qquad \Rightarrow \qquad \Psi(x,t) = \sum_{E,k} c_{E,k}(0)e^{-\mathrm{i}\frac{Et}{\hbar}}\varphi_{E,k}(x) \tag{3.12}$$

where $c_{E,k}(0) = \langle E,k|\Psi(0)\rangle$.

The possible eigenvalues E of the Hamiltonian $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$ satisfy an important inequality. Let $V_{\min} = \min_x V(x)$ be the minimum value of the function $V(x)$. Then

$$E \geq V_{\min}. \tag{3.13}$$

The proof of this inequality is straightforward. Let's assume, for the sake of contradiction, that there exists an eigenket $|E_0\rangle$ with energy $E_0 < V_{\min}$. Without loss of generality, we normalize the ket to 1, $\langle E_0|E_0\rangle = 1$. We would then have:

$$\begin{aligned} E_0 = \langle E_0|\hat{H}|E_0\rangle &= \langle E_0|\frac{\hat{p}^2}{2m}|E_0\rangle + \langle E_0|V(\hat{x})|E_0\rangle \\ &= \int dp\,\frac{p^2}{2m}|\langle E_0|p\rangle|^2 + \int dx\; V(x)|\langle E_0|x\rangle|^2 \\ &\geq \int dx\; V(x)|\langle E_0|x\rangle|^2 \geq V_{\min} \end{aligned} \tag{3.14}$$

in contradiction with the original assumption.

One last important observation. Not all functions that satisfy Eq. (3.11) belong to the Hilbert space generated by physical kets. *The Hilbert space for the eigenfunctions of the Hamiltonian operator is the space of continuous functions such that*

$$\boxed{\lim_{L\to\infty}\frac{1}{L}\int_{-L}^{L} dx\;|\varphi(x)|^2 < \infty} \tag{3.15}$$

So, if for a certain energy E we find a function $\varphi(x)$ that satisfies Eq. (3.11) but $\varphi(x)$ is not continuous or does not satisfy the condition in Eq. (3.15), then this function does not belong to the Hilbert space and therefore cannot be considered an eigenfunction.

3.1.1 Continuity Equation

An interesting consequence of the Schrödinger equation is the **continuity equation**. Let's see how to derive it and then discuss its physical significance. Multiply Eq. (3.10) on the left by $\Psi^*(x,t)$

$$\mathrm{i}\hbar\Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\Psi^*(x,t)\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x)|\Psi(x,t)|^2. \tag{3.16}$$

Let's now take the complex conjugate of this equation

$$-\mathrm{i}\hbar\Psi(x,t)\frac{\partial\Psi^*(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\Psi(x,t)\frac{\partial^2\Psi^*(x,t)}{\partial x^2} + V(x)|\Psi(x,t)|^2. \tag{3.17}$$

Subtracting Eq. (3.17) from Eq. (3.16) and, for brevity, omitting to write the dependence on x and t, we find

$$\mathrm{i}\hbar\left[\Psi^*\frac{\partial\Psi}{\partial t} + \Psi\frac{\partial}{\partial t}\Psi^*\right] = -\frac{\hbar^2}{2m}\left[\Psi^*\frac{\partial^2}{\partial x^2}\Psi - \Psi\frac{\partial^2}{\partial x^2}\Psi^*\right] \tag{3.18}$$

The term on the left can be rewritten as $\mathrm{i}\hbar\frac{\partial|\Psi|^2}{\partial t}$, while the term on the right can be rewritten as $-\frac{\hbar^2}{2m}\frac{\partial}{\partial x}\left[\Psi^*\frac{\partial\Psi}{\partial x} - \Psi\frac{\partial\Psi^*}{\partial x}\right]$. Dividing everything by $\mathrm{i}\hbar$, we then obtain:

$$\frac{\partial|\Psi|^2}{\partial t} + \frac{\hbar}{2m\mathrm{i}}\frac{\partial}{\partial x}\left[\Psi^*\frac{\partial\Psi}{\partial x} - \Psi\frac{\partial\Psi^*}{\partial x}\right] = 0. \tag{3.19}$$

Let's recall that $|\Psi(x,t)|^2 = P(x,t)$ is the probability density of finding the particle at position x, as discussed in Sect. 1.4. If we define the **probability current** as

$$\boxed{J(x,t) = \frac{\hbar}{2m\mathrm{i}}\left[\Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial x} - \Psi(x,t)\frac{\partial\Psi^*(x,t)}{\partial x}\right] = \frac{\hbar}{m}\mathrm{Im}\left[\Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial x}\right]} \tag{3.20}$$

we see that Eq. (3.19) has exactly the form of a continuity equation

$$\boxed{\frac{\partial P(x,t)}{\partial t} + \frac{\partial J(x,t)}{\partial x} = 0} \tag{3.21}$$

The physical meaning of this equation is clear. The probability of finding the particle between two points x_a and x_b is obtained by integrating $P(x,t)$ between x_a and x_b. When we do this, the continuity equation tells us that this probability varies with time as follows

$$\frac{\partial}{\partial t}\int_{x_a}^{x_b} dx\ P(x,t) = J(x_a,t) - J(x_b,t). \tag{3.22}$$

So, if the current entering at x_a is not balanced by the current exiting at x_b, the probability changes over time. Note that if the wave function is purely real, the current density is zero.

3.2 Piecewise Constant Potential

An important class of potentials for which it is possible to find all eigenfunctions analytically is the so-called *piecewise constant potentials*. They are characterized by a certain number of points $x_1 < x_2 < \cdots < x_N$ where they are discontinuous and are otherwise constant between two consecutive discontinuity points. So,

$$V(x) = \begin{cases} V_0 & x < x_1 \\ V_j & x_j < x < x_{j+1}, \quad j = 1, \ldots, N-1 \\ V_N & x > x_N \end{cases} \tag{3.23}$$

An example of a piecewise constant potential is illustrated in Fig. 3.1 where there are only two discontinuity points. We denote the region of the real axis where $V(x) = V_j$ as R_j, where $j = 0, \ldots, N$. Thus, $R_0 = (-\infty, x_1)$, $R_j = (x_j, x_{j+1})$ if $j = 1, \ldots, N-1$, and $R_N = (x_N, \infty)$. The set of all regions R_j is obviously the real axis itself.

In the case of a piecewise constant potential, the eigenvalue equation, see Eq. (3.11), can be decomposed into $N + 1$ equations, one for each region.

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V_j\right)\varphi_E(x) = E\varphi_E(x), \qquad x \in R_j. \tag{3.24}$$

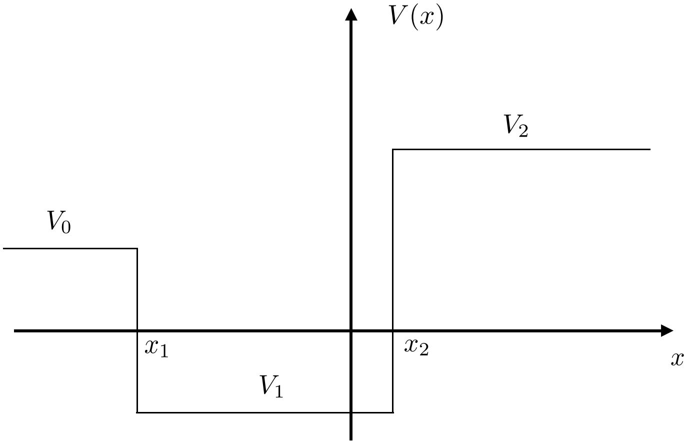


Fig. 3.1 An example of piecewice constant potential

We observe that *the eigenvalue E is the same in all regions*. At this moment, we omit the index k in the eigenfunction since we do not yet know the degeneracy of the eigenvalue E. We reintroduce it later if the degeneracy turns out to be greater than one. Since V_j is constant, i.e., independent of x, the most general solution of Eq. (3.24) is

$$\boxed{\varphi_E(x) = \begin{cases} A_j e^{\mathrm{i}q_j x} + B_j e^{-\mathrm{i}q_j x} & E \neq V_j \\ A_j + B_j x & E = V_j \end{cases}, \qquad x \in R_j} \tag{3.25}$$

where

$$q_j = \sqrt{\frac{2m}{\hbar^2}(E - V_j)}. \tag{3.26}$$

We observe that if $E > V_j$, then q_j is real, and therefore, in region R_j, the function $\varphi_E(x)$ is a linear combination of two purely imaginary exponentials. Conversely, if $E \leq V_j$, then $q_j = \mathrm{i}\sqrt{\frac{2m}{\hbar^2}(V_j - E)} \equiv \mathrm{i}k_j$ is imaginary, and in region R_j, the function $\varphi_E(x)$ is a linear combination of two purely real exponentials if $k_j > 0$, while it is a linear function of x if $k_j = 0$. In this case, a distinction is necessary. Indeed, if the region in question is region R_0, then for $x \in R_0$, Eq. (3.25) implies

$$\varphi_E(x) = \begin{cases} A_0 e^{-k_0 x} + B_0 e^{k_0 x} & E < V_0 \\ A_0 + B_0 x & E = V_0 \end{cases}, \qquad x \in R_0. \tag{3.27}$$

If the constant A_0 (for $E < V_0$) or the constant B_0 (for $E = V_0$) were nonzero, the eigenfunction could not satisfy the property in Eq. (3.15) because for $x \to -\infty$, the function $\varphi_E(x)$ diverges exponentially in the first case and linearly in the second case. Therefore, for the solution to belong to the Hilbert space, it is necessary to set $A_0 = 0$ if $E < V_0$ or $B_0 = 0$ if $E = V_0$:

$$\varphi_E(x) = \begin{cases} B_0 e^{k_0 x} & E < V_0 \\ A_0 & E = V_0 \end{cases}, \qquad x \in R_0. \tag{3.28}$$

Similarly, for $x \in R_N$, Eq. (3.25) implies

$$\varphi_E(x) = \begin{cases} A_N e^{-k_N x} + B_N e^{k_N x} & E < V_N \\ A_N + B_N x & E = V_N \end{cases}, \qquad x \in R_N \tag{3.29}$$

and if the constant B_N were nonzero, the eigenfunction could not satisfy the property in Eq. (3.15) as it would diverge exponentially (if $E < V_N$) or linearly (if $E = V_N$) for $x \to \infty$. Therefore, for the solution to belong to the Hilbert space, it is necessary to set $B_N = 0$:

$$\varphi_E(x) = \begin{cases} A_N e^{-k_N x} & E < V_N \\ A_N & E = V_N \end{cases}, \qquad x \in R_N. \tag{3.30}$$

The regions R_j in which the energy is less than the potential are called **classically forbidden regions** because classically the particle cannot be found in these regions. In quantum mechanics, however, there is a non-zero probability, proportional to $|\varphi_E(x)|^2$, of finding the particle there. Once again, we notice that the classical limit is recovered when $\hbar \to 0$. In this case, indeed, $k_j \to \infty$, and therefore, the condition in Eq. (3.15) imposes $A_j = 0$ if $x < 0$ and $B_j = 0$ if $x > 0$. Furthermore, if $x < 0$, we have $B_j e^{k_j x} \to 0$ as $k_j \to \infty$, while for $x > 0$, we have $A_j e^{-k_j x} \to 0$ as $k_j \to \infty$. In these regions, therefore, the probability of finding the particle is zero in the $\hbar \to 0$ limit.

As mentioned in Sect. 3.1, for $\varphi_E(x)$ to be a valid eigenfunction, in addition to satisfying the property in Eq. (3.15), it must also be a continuous function. The function $\varphi_E(x)$ in Eq. (3.25) is certainly continuous at all points except for the potential discontinuity points, namely, $x_1, \dots, x_N$. To ensure that $\varphi_E(x)$ is also continuous at those points, one must choose the constants A_j and B_j in such a way that they satisfy

$$\lim_{\epsilon \to 0} \varphi_E(x_j + \epsilon) = \lim_{\epsilon \to 0} \varphi_E(x_j - \epsilon), \qquad \forall x_j. \tag{3.31}$$

From the Schrödinger equation, we can also deduce a condition on the first derivative $\varphi'_E(x) = \frac{d}{dx}\varphi_E(x)$. Integrating Eq. (3.11) between $(x_j - \epsilon)$ and $(x_j + \epsilon)$, we find

$$\varphi'_E(x_j + \epsilon) - \varphi'_E(x_j - \epsilon) = -\frac{2m}{\hbar^2} \int_{x_j - \epsilon}^{x_j + \epsilon} dx\, [E - V(x)] \varphi_E(x). \tag{3.32}$$

In the limit $\epsilon \to 0$, the integral tends to zero because the integrand is finite for every x, and the integration domain tends to zero. Therefore, not only must the function itself be continuous, but also its first derivative

$$\lim_{\epsilon \to 0} \varphi'_E(x_j + \epsilon) = \lim_{\epsilon \to 0} \varphi'_E(x_j - \epsilon), \qquad \forall x_j. \tag{3.33}$$

Using the explicit form of $\varphi_E(x)$ in Eq. (3.25), the continuity conditions for the function and its derivative allow us to generate a linear and *homogeneous* system of $2N$ equations for the $N + 1$ unknown constants $A_0, \dots, A_N$ and the $N + 1$ unknown constants $B_0, \dots, B_N$, for a total of $2N + 2$ unknowns. The coefficients of this linear system depend on the energy E through the various q_j, as seen in Eq. (3.26).

Let's recall that an eigenket, and therefore an eigenfunction, is defined up to a multiplicative constant. This simply means that if φ_E is an eigenfunction with energy E, then $C\varphi_E$ is also an eigenfunction with energy E for any complex number C. Of course, in order to construct a basis, we should only consider linearly independent eigenfunctions. Therefore, without loss of generality, we can assign a certain value to one of the constants A_j or B_j. One possible choice could be $A_N = 1$, but any other choice at this level is equally valid. Fixing this constant uniquely determines the norm of the eigenfunction. For our purposes, we will refer to this "fixing" as the **condition on the norm**. The condition on the norm is equivalent to adding an additional equation, thus transforming the original homogeneous system of $2N$ equations for $2N + 2$ unknowns into a *non-homogeneous* system (the condition on the norm gives rise to a non-zero right-hand side) of $2N + 1$ equations for $2N + 2$ unknowns. Let's discuss the possible solutions.

To be concrete, let's consider the potential in Fig. 3.1. In this case, there are $N = 2$ discontinuity points, and the value of the potential in region $R_N = R_2$ is greater than the value of the potential in region R_0: $V_N = V_2 > V_0$.

(1) If the energy $E > V_2$, then E is also greater than V_0 since $V_2 > V_0$. In this case, we have no constraints on the unknown constants because neither the condition in Eq. (3.28) nor the condition in Eq. (3.30) is satisfied. We have a total of $2N + 2 = 6$ unknowns: A_0, B_0, A_1, B_1, A_2, B_2, and $2N = 4$ equations for the continuity of the eigenfunction and its derivative, plus the condition on the norm, for a total of $2N + 1 = 5$ equations. Therefore, the problem admits two linearly independent solutions that define two independent eigenfunctions with energy E: $\varphi_{E,1}$ and $\varphi_{E,2}$. In this case, the eigenvalue E is doubly degenerate. One way to ensure that we find two orthonormal solutions, and therefore linearly independent ones, is to solve the problem by choosing, first, the condition on the norm to be $A_0 = 1$ and imposing $B_N = B_2 = 0$. Then, solve the problem again with the condition on the norm to be $B_N = B_2 = 1$ and imposing $A_0 = 0$. So, in the first case, the eigenfunction in regions R_0 and R_2 takes the form:

$$\varphi_{E,1}(x) = \begin{cases} e^{\mathrm{i}q_0 x} + B_0 e^{-\mathrm{i}q_0 x} & x \in R_0 \\ A_2 e^{\mathrm{i}q_2 x} & x \in R_2 \end{cases} \tag{3.34}$$

whereas in the second case it takes the form

$$\varphi_{E,2}(x) = \begin{cases} B_0 e^{-\mathrm{i}q_0 x} & x \in R_0 \\ A_2 e^{\mathrm{i}q_2 x} + e^{-\mathrm{i}q_2 x} & x \in R_2 \end{cases} . \tag{3.35}$$

Now let's consider the continuity conditions for the function and its derivative. The continuity condition for the function at points x_1 and x_2 yields

$$\begin{aligned} A_0 e^{\mathrm{i}q_0 x_1} + B_0 e^{-\mathrm{i}q_0 x_1} &= A_1 e^{\mathrm{i}q_1 x_1} + B_1 e^{-\mathrm{i}q_1 x_1} \\ A_1 e^{\mathrm{i}q_1 x_2} + B_1 e^{-\mathrm{i}q_1 x_2} &= A_2 e^{\mathrm{i}q_2 x_2} + B_2 e^{-\mathrm{i}q_2 x_2} \end{aligned} \tag{3.36}$$

while the continuity condition for the derivative at points x_1 and x_2 yields

$$\begin{aligned} \mathrm{i}q_0 \left(A_0 e^{\mathrm{i}q_0 x_1} - B_0 e^{-\mathrm{i}q_0 x_1}\right) &= \mathrm{i}q_1 \left(A_1 e^{\mathrm{i}q_1 x_1} + B_1 e^{-\mathrm{i}q_1 x_1}\right) \\ \mathrm{i}q_1 \left(A_1 e^{\mathrm{i}q_1 x_2} + B_1 e^{-\mathrm{i}q_1 x_2}\right) &= \mathrm{i}q_2 \left(A_2 e^{\mathrm{i}q_2 x_2} + B_2 e^{-\mathrm{i}q_2 x_2}\right) \end{aligned} \tag{3.37}$$

To find the eigenfunction $\varphi_{E,1}$, we simply need to set $A_0 = 1$ and $B_2 = 0$ and use the four equations (3.36) and (3.37) to solve for B_0, A_1, B_1, A_2. To find the eigenfunction $\varphi_{E,2}$, we just need to set $A_0 = 0$ and $B_2 = 1$ and once again use the four equations (3.36) and (3.37) to solve for B_0, A_1, B_1, A_2.

If the potential had a generic number N of discontinuity points, the procedure would be exactly the same. To find two mutually orthonormal solutions, we would need to set $A_0 = 1$ and $B_N = 0$ for the eigenfunction $\varphi_{E,1}$ and $A_0 = 0$ and $B_N = 1$ for the eigenfunction $\varphi_{E,2}$. This way, the number of unknowns reduces from $2N + 2$ to $2N$, and we can use the $2N$ equations for the continuity of the function and its derivative to determine them.

If the value of the potential in region R_0 were greater than the value of the potential in region R_N, i.e., $V_0 > V_N$, the discussion remains entirely valid, but in that case, the energy E must be greater than V_0.

(2) If the energy is such that $V_N = V_2 \geq E > V_0$, then, as discussed under Eq. (3.29), we must add the additional equation $B_N = B_2 = 0$ to the system of equations; otherwise, the corresponding eigenfunction does not satisfy Eq. (3.15). In this case, the condition on the norm is chosen to be $A_0 = 1$, and thus, the eigenfunction in regions R_0 and R_2 takes the form

$$\varphi_E(x) = \begin{cases} e^{\mathrm{i}q_0 x} + B_0 e^{-\mathrm{i}q_0 x} & x \in R_0 \\ A_2 e^{-k_2 x} & x \in R_2 \end{cases} \tag{3.38}$$

We then have only 4 unknowns to determine, namely, B_0, A_1, B_1, A_2. To do this, we simply need to use the continuity conditions for the function and its derivative, which in this case provide:

$$\begin{aligned} e^{\mathrm{i}q_0 x_1} + B_0 e^{-\mathrm{i}q_0 x_1} &= A_1 e^{\mathrm{i}q_1 x_1} + B_1 e^{-\mathrm{i}q_1 x_1} \\ A_1 e^{\mathrm{i}q_1 x_2} + B_1 e^{-\mathrm{i}q_1 x_2} &= A_2 e^{-k_2 x_2} \end{aligned} \tag{3.39}$$

and

$$\begin{aligned} \mathrm{i}q_0 \left(e^{\mathrm{i}q_0 x_1} - B_0 e^{-\mathrm{i}q_0 x_1}\right) &= \mathrm{i}q_1 \left(A_1 e^{\mathrm{i}q_1 x_1} + B_1 e^{-\mathrm{i}q_1 x_1}\right) \\ \mathrm{i}q_1 \left(A_1 e^{\mathrm{i}q_1 x_2} + B_1 e^{-\mathrm{i}q_1 x_2}\right) &= -k_2 A_2 e^{-k_2 x_2} \end{aligned} \tag{3.40}$$

This system of equations admits only one solution, and therefore, there exists only one eigenfunction φ_E with energy E; in other words, the eigenvalue E is degenerate only once.

If the potential had a generic number N of discontinuity points, the procedure would be exactly the same. Simply impose the condition on the norm $A_0 = 1$ and the condition $B_N = 0$, which ensures that the eigenfunction belongs to the Hilbert space of physical solutions, see again Eq. (3.30). This way, the number of unknowns reduces from $2N + 2$ to $2N$, and we can use the $2N$ equations for the continuity of the function and its derivative to determine them.

If the value of the potential in region R_0 were greater than the value of the potential in region R_N, i.e., $V_0 > V_N$, the discussion we just had remains valid provided that we exchange region R_0 with region R_N. So, if the energy E satisfies $V_0 \geq E > V_N$, the condition on the norm becomes $B_N = 1$, while the property in Eq. (3.15) implies that either $A_0 = 0$ if $E < V_0$ or $B_0 = 0$ if $E = V_0$, as seen again in Eq. (3.28). In any case, the number of unknowns reduces from $2N + 2$ to $2N$, and we can use the $2N$ equations for the continuity of the function and its derivative to determine them.

(3) If the energy $E \leq V_0$, as seen in Eq. (3.13), there are no solutions with energy $E < V_0$ when $V_0 = V_{\text{min}}$. However, we could have solutions with energy between V_{min} and V_0 if $V_0 \geq V_{\text{min}}$. This is precisely the case for the potential in Fig. 3.1 because $V_0 > V_1 = V_{\text{min}}$. As discussed under Eqs. (3.27) and (3.29), for these energies, the physical eigenfunctions are characterized by the condition $A_0 = 0$ if $E < V_0$ or $B_0 = 0$ if $E = V_0$ for the region R_0 and by the condition $B_N = B_2 = 0$ in the region $R_N = R_2$. We also need to choose a condition for the norm; for example, let's choose $A_2 = 1$. So, in the case of $E < V_0$, we have $A_0 = B_2 = 0$ and $A_2 = 1$. This leaves us with only 3 unknowns: B_0, A_1, B_1 to satisfy the $2N = 4$ equations for the continuity of the function and its derivative. Similarly, if we consider the case of $E = V_0$, we have $B_0 = B_2 = 0$ and $A_2 = 1$, and we still have only 3 unknowns: A_0, A_1, B_1 to satisfy the $2N = 4$ equations for the continuity of the function and its derivative. Since the number of equations exceeds the number of unknowns, there are generally no solutions at these energies unless... one of the equations in the system is a linear combination of the others. This could happen for some special values of the energy E. The set of special energies for which a solution still exists can be either empty (no eigenstates with energy $E < V_0$) or a set consisting of a finite number of energies or a set consisting of a countably infinite number of energies. The case of $E < V_0$ represents the first example of **energy quantization**. Unlike the classical case, not all energies between V_{min} and V_0 are possible. Eigenfunctions with energies $E < V_0$ are called **bound states**. The term "bound states" comes from the fact that the eigenfunctions tend to zero exponentially as $x \to \pm\infty$, and therefore, the probability of finding the particle is maximum near the potential well. In other words, the potential well tends to bind the particle.

Let's see explicitly how to deal with the case of Fig. 3.1. For $E < V_0$, the continuity conditions for the function and its derivative yield:

$$\begin{aligned} B_0 e^{k_0 x_1} &= A_1 e^{\mathrm{i} q_1 x_1} + B_1 e^{-\mathrm{i} q_1 x_1} \\ A_1 e^{\mathrm{i} q_1 x_2} + B_1 e^{-\mathrm{i} q_1 x_2} &= e^{-k_2 x_2} \end{aligned} \tag{3.41}$$

and

$$\begin{aligned} k_0 B_0 e^{k_0 x_1} &= \mathrm{i} q_1 \left(A_1 e^{\mathrm{i} q_1 x_1} - B_1 e^{-\mathrm{i} q_1 x_1} \right) \\ \mathrm{i} q_1 \left(A_1 e^{\mathrm{i} q_1 x_2} - B_1 e^{-\mathrm{i} q_1 x_2} \right) &= -k_2 e^{-k_2 x_2} \end{aligned} \tag{3.42}$$

We can represent this system in matrix form as follows:

Table 3.1 Mathematical form of the eigenfunctions (last three columns) for different possible energies (first column) for a piecewise constant potential with $V_N \geq V_0$. The second column indicates the degeneracy

$V_N \geq V_0$	Degeneracy	$x \in R_0$	$x \in R_N$	$x \in R_j, \quad j \neq 0, N$
$E > V_N$	2	$e^{\mathrm{i}q_0x} + B_0e^{-\mathrm{i}q_0x}$	$A_Ne^{\mathrm{i}q_Nx}$	$A_je^{\mathrm{i}q_jx} + B_je^{-\mathrm{i}q_jx}$ if $E > V_j$ $A_j + B_jx$ if $E = V_j$ $A_je^{-k_jx} + B_je^{k_jx}$ if $E < V_j$
		$B_0e^{-\mathrm{i}q_0x}$	$A_Ne^{\mathrm{i}q_Nx} + e^{-\mathrm{i}q_Nx}$	
$V_0 \leq E \leq V_N$	1	$e^{\mathrm{i}q_0x} + B_0e^{-\mathrm{i}q_0x}$	$A_Ne^{-k_Nx}$	
$V_{\min} \leq E < V_0$	1	$B_0e^{k_0x}$	e^{-k_Nx}	

$$\begin{pmatrix} e^{k_0x_1} & -e^{\mathrm{i}q_1x_1} & -e^{-\mathrm{i}q_1x_1} \\ 0 & e^{\mathrm{i}q_1x_2} & e^{-\mathrm{i}q_1x_2} \\ k_0e^{k_0x_1} & -\mathrm{i}q_1e^{\mathrm{i}q_1x_2} & \mathrm{i}q_1e^{-\mathrm{i}q_1x_1} \\ 0 & \mathrm{i}q_1e^{\mathrm{i}q_1x_2} & -\mathrm{i}q_1e^{-\mathrm{i}q_1x_2} \end{pmatrix} \begin{pmatrix} B_0 \\ A_1 \\ B_1 \end{pmatrix} = \begin{pmatrix} 0 \\ e^{-k_2x_2} \\ 0 \\ -k_2e^{-k_2x_2} \end{pmatrix} \tag{3.43}$$

This system has a solution only if the determinant of the matrix, obtained by adding the coumn vector on the right-hand side of the equality, is zero. In other words:

$$\mathrm{Det} \begin{pmatrix} e^{k_0x_1} & -e^{\mathrm{i}q_1x_1} & -e^{-\mathrm{i}q_1x_1} & 0 \\ 0 & e^{\mathrm{i}q_1x_2} & e^{-\mathrm{i}q_1x_2} & e^{-k_2x_2} \\ k_0e^{k_0x_1} & -\mathrm{i}q_1e^{\mathrm{i}q_1x_2} & \mathrm{i}q_1e^{-\mathrm{i}q_1x_1} & 0 \\ 0 & \mathrm{i}q_1e^{\mathrm{i}q_1x_2} & -\mathrm{i}q_1e^{-\mathrm{i}q_1x_2} & -k_2e^{-k_2x_2} \end{pmatrix} = 0. \tag{3.44}$$

The solutions to this equation provide the discrete energies at which bound states can exist.

If the potential has a generic number of N discontinuity points, the procedure would be exactly the same. By imposing $A_0 = 0$ for $E < V_0$ or $B_0 = 0$ for $E = V_0$ in region R_0, $B_N = 0$ in region R_N, and choosing the condition on the norm to be, for example, $A_N = 1$, the number of unknowns reduces from $2N + 2$ to $2N - 1$. Therefore, a solution to the system of $2N$ equations exists only if one of the equations can be written as a linear combination of the others.

In Table 3.1, we summarize what has been discussed so far. This table shows the form of the eigenfunctions (last three columns) for different possible energies (first column) in various regions, for the case $V_N \geq V_0$.

3.3 Piecewise Constant Potential with Dirac Deltas

It is possible to calculate exactly the eigenstates of the Hamiltonian even when we add, in some places, Dirac delta functions to a constant potential. The procedure is indeed identical to that discussed in the previous section, except for a very small difference. Let's see it.

We denote by $x_1 < x_2 < \cdots x_N$ the points at which the potential $V(x)$ is discontinuous or contains a Dirac delta, or both. This means that for $x_{j-1} < x < x_{j+1}$, the potential has the following form:

$$V(x) = a_j \delta(x - x_j) + \begin{cases} V_{j-1} & x < x_j \\ V_j & x > x_j \end{cases} \tag{3.45}$$

If $a_j = 0$ and $V_{j-1} \neq V_j$, then at x_j, the potential is simply discontinuous, just as before. If $a_j \neq 0$ and $V_{j-1} = V_j$, then the potential contains a Dirac delta at x_j, and its value is the same on both sides of x_j. Finally, if $a_j \neq 0$ and $V_{j-1} \neq V_j$, then the potential contains a Dirac delta at x_j and has different values on the left and right sides of x_j. In any case, the potential is a constant equal to V_j in the region $R_j = (x_j, x_{j+1})$. Therefore, in the region R_j, the Schrödinger equation is once again given by Eq. (3.24), and the most general solution is exactly the same as before

$$\varphi_E(x) = \begin{cases} A_j e^{\mathrm{i} q_j x} + B_j e^{-\mathrm{i} q_j x} & E \neq V_j \\ A_j + B_j x & E = V_j \end{cases}, \qquad x \in R_j \tag{3.46}$$

where

$$q_j = \sqrt{\frac{2m}{\hbar^2}(E - V_j)}. \tag{3.47}$$

To calculate the constants A_j and B_j, we can proceed in the same way as before, except for the fact that we need to modify the continuity condition for the derivative. Let us reconsider Eq. (3.32). Regardless of the value of ϵ, we have

$$\int_{x_j - \epsilon}^{x_j + \epsilon} a_j \delta(x - x_j) \varphi_E(x) = a_j \varphi_E(x_j) \tag{3.48}$$

and hence

$$\lim_{\epsilon \to 0} [\varphi'_E(x_j + \epsilon) - \varphi'_E(x_j - \epsilon)] = \frac{2m a_j}{\hbar^2} \varphi_E(x_j) \qquad \forall x_j\ . \tag{3.49}$$

If $a_j = 0$, which means in the absence of the Dirac delta, we recover the continuity condition for the first derivative. Conversely, we should impose the condition for the discontinuity of the first derivative, as given by Eq. (3.49). Since we have N

points x_j, Eq. (3.49) provides N equations, and we can proceed exactly as before to determine the eigenfunctions.

One final observation. The value $\varphi_E(x_j)$ of the eigenfunction at x_j is unique and well-defined because the eigenfunction is continuous. We can express this value using either the form of the eigenfunction in $R_{j-1} = (x_{j-1}, x_j)$ and then setting $x = x_j$ or the form of the eigenfunction in $R_j = (x_j, x_{j+1})$ and then setting $x = x_j$. The continuity condition at x_j ensures that the result remains unchanged.

3.4 Reflection and Transmission Coefficients

Let us consider a piecewise constant potential with or without Dirac deltas. We have seen that for energies E greater than both V_0 and V_N, there exist two eigenfunctions of energy E, and these eigenfunctions in the regions R_0 and R_N take the form in Eqs. (3.34) and (3.35). Let us focus on Eq. (3.34), as the same considerations apply to the other equation. It is very common to denote the coefficient B_0 with the letter $\mathcal{R}$ and the coefficient A_N with the letter $\mathcal{T}$, so:

$$\varphi_{E,1}(x) = \begin{cases} e^{\mathrm{i}q_0x} + \mathcal{R}\, e^{-\mathrm{i}q_0x} & x \in R_0 \\ \mathcal{T}\, e^{\mathrm{i}q_Nx} & x \in R_N \end{cases} \tag{3.50}$$

As we know, the plane wave $e^{\mathrm{i}q_0x}$ is proportional to the scalar product between a position eigenket and a momentum eigenket with an eigenvalue of $\hbar q_0$. Therefore, we can interpret the state of the electron in region R_0 as an electron with momentum $\hbar q_0 > 0$ moving from left to right and, with a probability proportional to $|\mathcal{R}|^2$, being reflected as an electron with momentum $-\hbar q_0$ moving from right to left. Similarly, we can interpret the state of the electron in region R_N as an electron that, with a probability proportional to $|\mathcal{T}|^2$, is transmitted into this region with momentum $\hbar q_N > 0$ and thus moves from left to right. Due to this physical interpretation, the coefficients $\mathcal{R}$ and $\mathcal{T}$ are called the **reflection coefficient** and **transmission coefficient**, respectively.

We want to use the continuity equation to derive an exact relationship between the reflection and transmission coefficients. Since the eigenfunction does not depend on time, it follows that neither the probability density nor the probability current depends on time. Furthermore, from Eq. (3.21), we also deduce that $J(x)$ must be independent of x. Calculating J in the region R_0, we find

$$J = \frac{\hbar}{m} q_0 (1 - |\mathcal{R}|^2), \tag{3.51}$$

whereas if J is calculated in region R_N we find

$$J = \frac{\hbar}{m} q_N |\mathcal{T}|^2. \tag{3.52}$$

Equating these two results we obtain the sought relation

$$\boxed{q_0(1 - |\mathcal{R}|^2) = q_N|\mathcal{T}|^2} \tag{3.53}$$

It is interesting to note that if $V_0 = V_N$, then $q_0 = q_N$, as seen in Eq. (3.26), and the relationship above becomes:

$$\boxed{|\mathcal{R}|^2 + |\mathcal{T}|^2 = 1} \tag{3.54}$$

The physical interpretation of this result is transparent. The probability that an incident electron may be reflected, when summed with the probability that it may be transmitted, equals 1. A similar reasoning can be applied to the eigenfunction $\varphi_{E,2}$ by identifying the reflection coefficient with A_N and the transmission coefficient with B_0.

3.5 Harmonic Potential

Let us consider a quantum spring with spring constant k, one end attached to the origin of coordinates, and the other end connected to a particle of mass m free to move along the x-axis. Denoting the position of the particle as l and the rest length of the spring as l_0, the particle experiences a force given by $F(x) = -\frac{d}{dx}V(x)$, where the distance x is defined as $x = l - l_0$, and

$$V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2x^2 \tag{3.55}$$

is the potential energy of the particle. In Eq. (3.55), we define the angular frequency $\omega \equiv \sqrt{\frac{k}{m}}$. Therefore, the Hamiltonian of the system is:

$$\boxed{\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 = \hbar\omega\left(\frac{\hat{p}^2}{2m\hbar\omega} + \frac{m\omega}{2\hbar}\hat{x}^2\right)} \tag{3.56}$$

This Hamiltonian is known as the Hamiltonian of the **harmonic oscillator**. Just like all quadratic forms of the type $u^2 + v^2$ can be written as $(u + iv)(u - iv)$, let us try to rewrite the Hamiltonian of the harmonic oscillator using the *non-Hermitian operators*

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + \mathrm{i}\frac{\hat{p}}{\sqrt{2m\hbar\omega}}, \tag{3.57a}$$

$$\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} - \mathrm{i}\frac{\hat{p}}{\sqrt{2m\hbar\omega}}, \tag{3.57b}$$

from which it follows that

$$\hat{p} = \sqrt{2m\hbar\omega}\,\frac{\hat{a} - \hat{a}^\dagger}{2\mathrm{i}}, \tag{3.58a}$$

$$\hat{x} = \sqrt{\frac{2\hbar}{m\omega}}\,\frac{\hat{a} + \hat{a}^\dagger}{2}. \tag{3.58b}$$

Of course, unlike ordinary complex numbers, $\hat{a}$ and $\hat{a}^\dagger$ do not commute. Remembering that (sixth postulate) $[\hat{x}, \hat{p}] = \mathrm{i}\hbar$, we find

$$[\hat{a}, \hat{a}^\dagger] = -\frac{\mathrm{i}}{2\hbar}[\hat{x}, \hat{p}] + \frac{\mathrm{i}}{2\hbar}[\hat{p}, \hat{x}] = 1 \tag{3.59}$$

Therefore

$$\frac{\hat{p}^2}{2m\hbar\omega} + \frac{m\omega}{2\hbar}\hat{x}^2 = \frac{1}{4}\left(\hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a} + \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a}\right) = \frac{1}{2}\left(\hat{a}^\dagger\hat{a} + \hat{a}\hat{a}^\dagger\right) = \hat{a}^\dagger\hat{a} + \frac{1}{2}. \tag{3.60}$$

We can then rewrite the Hamiltonian in the following compact form:

$$\boxed{\hat{H} = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)} \tag{3.61}$$

3.5.1 Raising and Lowering Operators

The operators $\hat{a}$ and $\hat{a}^\dagger$ allow us to compute all the eigenstates of $\hat{H}$ from the knowledge of a single eigenstate. To demonstrate this, we notice that from the commutation rule in Eq. (3.59), it follows that

$$[\hat{a}^\dagger\hat{a}, \hat{a}] = \hat{a}^\dagger[\hat{a}, \hat{a}] + [\hat{a}^\dagger, \hat{a}]\hat{a} = -\hat{a}, \tag{3.62}$$

$$[\hat{a}^\dagger\hat{a}, \hat{a}^\dagger] = \hat{a}^\dagger[\hat{a}, \hat{a}^\dagger] + [\hat{a}^\dagger, \hat{a}^\dagger]\hat{a} = \hat{a}^\dagger. \tag{3.63}$$

Let $|\lambda\rangle$ be the normalized eigenstates, meaning $\langle\lambda|\lambda\rangle = 1$, of $\hat{a}^\dagger\hat{a}$ with an eigenvalue λ and, therefore, of $\hat{H}$ with an eigenvalue $\hbar\omega\left(\lambda + \frac{1}{2}\right)$:

$$\hat{a}^\dagger\hat{a}|\lambda\rangle = \lambda|\lambda\rangle \qquad \Rightarrow \qquad \hat{H}|\lambda\rangle = \hbar\omega(\lambda + \frac{1}{2})|\lambda\rangle. \tag{3.64}$$

Let us try to understand the possible values of λ. It turns out that

$$\hat{a}^\dagger \hat{a}\, \hat{a}^\dagger |\lambda\rangle = [\hat{a}^\dagger \hat{a}, \hat{a}^\dagger]|\lambda\rangle + \lambda \hat{a}^\dagger |\lambda\rangle = (\lambda + 1)\hat{a}^\dagger |\lambda\rangle, \tag{3.65}$$

and

$$\hat{a}^\dagger \hat{a}\, \hat{a}|\lambda\rangle = [\hat{a}^\dagger \hat{a}, \hat{a}]|\lambda\rangle + \lambda \hat{a}|\lambda\rangle = (\lambda - 1)\hat{a}|\lambda\rangle. \tag{3.66}$$

So, the ket $\hat{a}^\dagger|\lambda\rangle$ and the ket $\hat{a}|\lambda\rangle$ are eigenstates of $\hat{a}^\dagger\hat{a}$ with eigenvalues $\lambda + 1$ and $\lambda - 1$, respectively. For this reason, the operator $\hat{a}^\dagger$ is called the **raising operator**, and the operator $\hat{a}$ is called the **lowering operator**. Not yet knowing if these kets are normalized to unity, we can write:

$$\hat{a}^\dagger|\lambda\rangle = \alpha_\lambda|\lambda + 1\rangle \qquad \hat{a}|\lambda\rangle = \beta_\lambda|\lambda - 1\rangle. \tag{3.67}$$

Calculating the proportionality coefficients is quickly done

$$|\alpha_\lambda|^2 = \langle\lambda|\hat{a}\hat{a}^\dagger|\lambda\rangle = \langle\lambda|[\hat{a}, \hat{a}^\dagger] + \hat{a}^\dagger\hat{a}|\lambda\rangle = \lambda + 1 \tag{3.68}$$

$$|\beta_\lambda|^2 = \langle\lambda|\hat{a}^\dagger\hat{a}|\lambda\rangle = \lambda \tag{3.69}$$

Therefore

$$\boxed{\hat{a}^\dagger|\lambda\rangle = \sqrt{\lambda + 1}|\lambda + 1\rangle \qquad \hat{a}|\lambda\rangle = \sqrt{\lambda}|\lambda - 1\rangle} \tag{3.70}$$

The second of these last two relationships is particularly important. Equation (3.69) holds for all eigenvalues λ; therefore, all eigenvalues must be non-negative because the squared modulus of a complex number, such as $|\beta_\lambda|^2$, is greater than or equal to zero. Let $\lambda_{\text{min}} \geq 0$ be the smallest eigenvalue. The second relation in Eq. (3.70) tells us that $\hat{a}|\lambda_{\text{min}}\rangle$ is an eigenket with an eigenvalue of $\lambda_{\text{min}} - 1$, which is absurd, considering that λ_{min} is the smallest eigenvalue. The only way out from this contradiction is for $\lambda_{\text{min}} = 0$. In this case, indeed, $\hat{a}|0\rangle = \sqrt{0}| - 1\rangle = |\emptyset\rangle$, which means the action of $\hat{a}$ on the ket $|0\rangle$ produces the null ket $|\emptyset\rangle$, which is not a physical state as it has zero norm (the representation of the null ket is, regardless of the basis, a vector with all components equal to zero).

We conclude that the lowest eigenvalue of $\hat{a}^\dagger\hat{a}$ is zero, and in accordance with the introduced notation, we denote the corresponding eigenket as $|0\rangle$. All other eigenkets and eigenvalues of $\hat{a}^\dagger\hat{a}$ can be obtained using the raising operator. From the first of Eq. (3.70), we have:

$$\begin{aligned}
|1\rangle &= \frac{\hat{a}^\dagger}{\sqrt{1}}|0\rangle \\
|2\rangle &= \frac{\hat{a}^\dagger}{\sqrt{2}}|1\rangle = \frac{(\hat{a}^\dagger)^2}{\sqrt{2!}}|0\rangle \\
|3\rangle &= \frac{\hat{a}^\dagger}{\sqrt{3}}|2\rangle = \frac{(\hat{a}^\dagger)^3}{\sqrt{3!}}|0\rangle
\end{aligned} \tag{3.71}$$

and more generally

$$\boxed{|n\rangle = \frac{(\hat{a}^\dagger)^n}{\sqrt{n!}}|0\rangle} \tag{3.72}$$

where $n = 0, 1, 2, 3, \ldots$.

The kets $|n\rangle$ are also eigenkets of the Hamiltonian, as it follows from Eq. (3.64),

$$\boxed{\hat{H}|n\rangle = \hbar\omega(n + \frac{1}{2})|n\rangle} \tag{3.73}$$

The possible eigenvalues of the Hamiltonian represent the possible measurements of energy, and from Eq. (3.73), we see that they do not form a continuous spectrum. The harmonic oscillator is the second example of a system where the energy is *quantized*. The ground state of the harmonic oscillator is the ket $|0\rangle$. It is indeed the eigenket with the lowest eigenvalue, which is $\hbar\omega/2 > 0$. Classically, the minimum energy is obtained when the particle is at rest (zero momentum) at the potential minimum ($x = 0$). As we have seen in Sect. 1.8, such a state is not compatible with Heisenberg's uncertainty principle, as both the position and momentum values would be simultaneously known without any uncertainty. The classical result is recovered if Planck's constant were zero, i.e., $\hbar = 0$.

We can easily verify that Heisenberg's uncertainty principle is satisfied for any eigenket of $\hat{H}$. Since eigenkets with different energies are orthogonal to each other, the mean values of $\hat{x}$ and $\hat{p}$ are zero. Indeed:

$$\langle n|\hat{x}|n\rangle = \sqrt{\frac{2\hbar}{m\omega}}\,\langle n|\frac{\hat{a}+\hat{a}^\dagger}{2}|n\rangle = 0 \tag{3.74}$$

$$\langle n|\hat{p}|n\rangle = \sqrt{2m\hbar\omega}\,\langle n|\frac{\hat{a}-\hat{a}^\dagger}{2\mathrm{i}}|n\rangle = 0 \tag{3.75}$$

since $\hat{a}|n\rangle$ generates a ket proportional to $|n-1\rangle$ and $\hat{a}^\dagger|n\rangle$ generates a ket proportional to $|n+1\rangle$. For the squares, we have

$$\langle n|\hat{x}^2|n\rangle = \frac{2\hbar}{m\omega}\langle n|\left(\frac{\hat{a}+\hat{a}^\dagger}{2}\right)^2|n\rangle = \frac{2\hbar}{m\omega}\langle n|\frac{\hat{a}\hat{a}^\dagger+\hat{a}^\dagger\hat{a}}{4}|n\rangle = \frac{\hbar}{m\omega}\left(n+\frac{1}{2}\right) \tag{3.76}$$

$$\langle n|\hat{p}^2|n\rangle = 2m\hbar\omega\langle n|\left(\frac{\hat{a}-\hat{a}^\dagger}{2\mathrm{i}}\right)^2|n\rangle = 2m\hbar\omega\langle n|\frac{\hat{a}\hat{a}^\dagger+\hat{a}^\dagger\hat{a}}{4}|n\rangle = m\hbar\omega\left(n+\frac{1}{2}\right) \tag{3.77}$$

where it has been taken into account that $\hat{a}^2|n\rangle$ generates a ket proportional to $|n-2\rangle$, and $(\hat{a}^\dagger)^2|n\rangle$ generates a ket proportional to $|n+2\rangle$. In conclusion, the product of the position and momentum variances is given by

$$\boxed{\langle n|\hat{\sigma}_x^2|n\rangle\langle n|\hat{\sigma}_p^2|n\rangle = \hbar^2(n+\frac{1}{2})^2 \geq \frac{\hbar^2}{4}} \tag{3.78}$$

in accordance with Eq. (1.173). In particular, Heisenberg's uncertainty principle is saturated (i.e., the equality sign holds) only for the ground state $n = 0$.

3.5.2 Eigenfunctions and Hermite Polynomials

In this section, we want to explicitly calculate the form of the eigenfunctions $\Psi_n(x) = \langle x|n\rangle$ of the Hamiltonian, which is the inner product between a position bra and an eigenket of the Hamiltonian. This allows us to know the probability density of finding the particle at x when it is prepared in an eigenket of the Hamiltonian. From $\hat{a}|0\rangle = |\emptyset\rangle$, it follows that

$$\begin{aligned}\langle x|\hat{a}|0\rangle &= \langle x|\sqrt{\frac{m\omega}{2\hbar}}\hat{x} + \mathrm{i}\frac{\hat{p}}{\sqrt{2m\hbar\omega}}|0\rangle \\ &= \sqrt{\frac{m\omega}{2\hbar}}x\Psi_0(x) + \sqrt{\frac{\hbar}{2m\omega}}\frac{d}{dx}\Psi_0(x) = 0 \end{aligned}\tag{3.79}$$

where we use Eq. (3.3). Therefore, the eigenfunction of the ground state satisfies the first-order homogeneous differential equation

$$\Psi_0'(x) + \frac{m\omega}{\hbar}x\Psi_0(x) = 0, \tag{3.80}$$

whose solution is a Gaussian $\Psi_0(x) = Ce^{-\frac{m\omega}{2\hbar}x^2}$ with width

$$x_0 \equiv \sqrt{\frac{\hbar}{m\omega}}. \tag{3.81}$$

We can determine the constant C from the normalization $\langle n|n\rangle = 1$. We have

$$1 = \langle 0|0\rangle = \int dx\langle 0|x\rangle\langle x|0\rangle = \int dx|\Psi_0(x)|^2 = |C|^2\sqrt{\frac{\pi\hbar}{m\omega}}. \tag{3.82}$$

Hence

$$\boxed{\Psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2} = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{x^2}{2x_0^2}}} \tag{3.83}$$

To obtain all the other eigenfunctions of the Hamiltonian, we can use Eq. (3.72). We rewrite the operator $\hat{a}^\dagger$ in Eq. (3.57) in terms of the width x_0:

$$\hat{a}^\dagger = \frac{1}{\sqrt{2}}\left(\frac{\hat{x}}{x_0} - \mathrm{i}\frac{x_0\hat{p}}{\hbar}\right) \tag{3.84}$$

Taking the inner product with the bra $\langle x|$, we have

$$\begin{aligned}\Psi_1(x) = \langle x|1\rangle = \langle x|\hat{a}^\dagger|0\rangle &= \frac{1}{\sqrt{2}}\langle x|\frac{\hat{x}}{x_0} - \mathrm{i}\frac{x_0\hat{p}}{\hbar}|0\rangle \\ &= \frac{1}{\sqrt{2}}\left(\frac{x}{x_0} - x_0\frac{d}{dx}\right)\Psi_0(x).\end{aligned} \tag{3.85}$$

It is convenient to define the dimensionless variable $\bar{x} = x/x_0$. Then

$$\begin{aligned}\Psi_1(x) &= \frac{1}{\sqrt{2}}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\left(\bar{x} - \frac{d}{d\bar{x}}\right)e^{-\frac{\bar{x}^2}{2}} \\ &= \frac{1}{\sqrt{2}}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4} 2\bar{x}\, e^{-\frac{\bar{x}^2}{2}},\end{aligned} \tag{3.86}$$

Knowing $\Psi_1(x)$ we can then obtain $\Psi_2(x)$:

$$\begin{aligned}\Psi_2(x) = \langle x|2\rangle = \frac{1}{\sqrt{2}}\langle x|\hat{a}^\dagger|1\rangle &= \frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\langle x|\frac{\hat{x}}{x_0} - \mathrm{i}\frac{x_0\hat{p}}{\hbar}|1\rangle \\ &= \frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\left(\bar{x} - \frac{d}{d\bar{x}}\right)\Psi_1(x) \\ &= \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\left(4\bar{x}^2 - 2\right)e^{-\frac{\bar{x}^2}{2}}.\end{aligned} \tag{3.87}$$

It is easy to convince oneself that the general structure of the eigenfunctions is

$$\boxed{\Psi_n(x) = \frac{1}{\sqrt{2^n n!}}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4} H_n(\bar{x})e^{-\frac{\bar{x}^2}{2}}} \tag{3.88}$$

where $H_n(\bar{x})$ is a polynomial of degree n in $\bar{x}$. In particular, H_n contains only even powers if n is even and only odd powers if n is odd. These polynomials are called **Hermite polynomials**. In addition to the ones we have already found, here are some others:

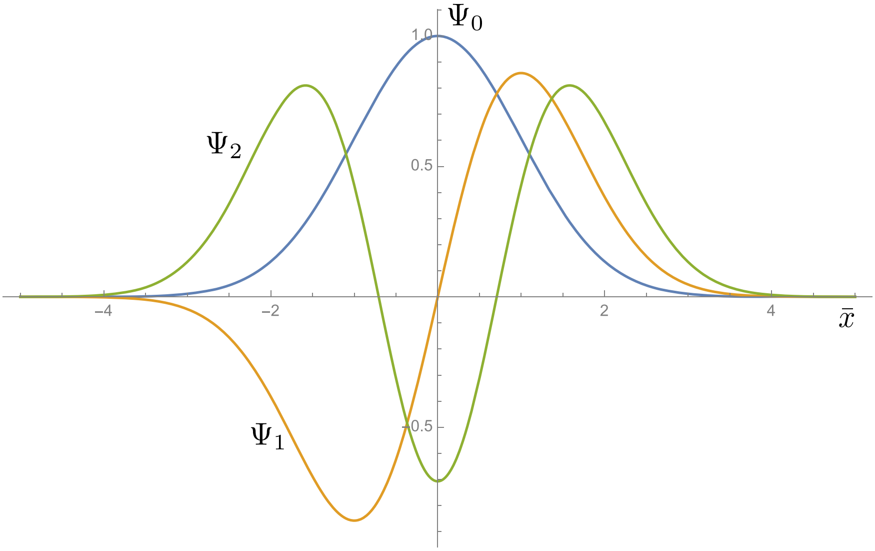


Fig. 3.2 The first three eigenfunctions of the harmonic oscillator

$$
\begin{aligned}
H_0(\bar{x}) &= 1\\
H_1(\bar{x}) &= 2\bar{x}\\
H_2(\bar{x}) &= 4\bar{x}^2 - 2\\
H_3(\bar{x}) &= 8\bar{x}^3 - 12\bar{x}\\
H_4(\bar{x}) &= 16\bar{x}^4 - 48\bar{x}^2 + 12\\
H_5(\bar{x}) &= 32\bar{x}^5 - 160\bar{x}^3 + 120\bar{x}\\
H_6(\bar{x}) &= 64\bar{x}^6 - 480\bar{x}^4 + 720\bar{x}^2 - 120.
\end{aligned}
\tag{3.89}
$$

In Fig. 3.2, we show the behavior of the first three eigenfunctions of the harmonic oscillator. It can be observed that if the particle is in the ground state Ψ_0, the probability density is maximum at the origin and then decreases as we move away from it. The particle in the first excited state has zero probability of being at the origin, consistent with the fact that the Hermite polynomial H_1 is an odd function. More generally, the wavefunction of the nth excited state exhibits n nodes, meaning n values of x where the probability density is zero.

3.5.3 Coherent States

We have shown that the average value of position and momentum is zero if the particle is in an eigenstate of the Hamiltonian, see Eqs. (3.74) and (3.75). Furthermore, as discussed below Eq. (1.153), the average value of an operator is time-independent if the initial state is an eigenstate of the Hamiltonian. Therefore, the average values of position and momentum continue to be zero if the initial state is one of the kets $|n\rangle$. However, classically, a particle attached to a spring is described by an oscillatory trajectory $x(t) = A\cos(\omega t - \phi)$ and thus by an oscillating momentum $p = m\dot{x}(t)$. This means that to recover the classical result, the initial state cannot be an eigenstate of $\hat{H}$. In this section, we find out how the initial state should be prepared so that the average values of position and momentum behave as in the classical case.

Consider the lowering operator $\hat{a}$ and denote by $|\Phi_\gamma\rangle$ one of its eigenkets with eigenvalue γ, normalized to one:

$$\hat{a}|\Phi_\gamma\rangle = \gamma|\Phi_\gamma\rangle, \qquad \langle\Phi_\gamma|\Phi_\gamma\rangle = 1. \tag{3.90}$$

Since $\hat{a}$ is not Hermitian, the eigenvalue γ can also be complex. We want to show that

$$|\Phi_\gamma\rangle = C\, e^{\gamma\hat{a}^\dagger}|0\rangle \tag{3.91}$$

where C is a normalization constant that we determine later, and $|0\rangle$ is the eigenket with the lowest energy of the harmonic oscillator. The proof is quite simple. We define the commutator

$$\hat{Q}_n = [\hat{a}, (\hat{a}^\dagger)^n] \tag{3.92}$$

Using the identity $[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]$ with $\hat{A} = \hat{a}$, $\hat{B} = \hat{a}^\dagger$, and $\hat{C} = (\hat{a}^\dagger)^{n-1}$, we can proceed as we did in Eq. (1.119) and find

$$\hat{Q}_n = (\hat{a}^\dagger)^{n-1} + \hat{a}^\dagger\hat{Q}_{n-1} = n(\hat{a}^\dagger)^{n-1}. \tag{3.93}$$

So, keeping in mind that $\hat{a}|0\rangle = |\emptyset\rangle$,

$$\begin{aligned}\hat{a}|\Phi_\gamma\rangle &= C\,\hat{a}e^{\gamma\hat{a}^\dagger}|0\rangle = C\sum_{n=0}^{\infty}\frac{\gamma^n}{n!}\hat{a}(\hat{a}^\dagger)^n|0\rangle = C\sum_{n=0}^{\infty}\frac{\gamma^n}{n!}\hat{Q}_n|0\rangle = C\sum_{n=0}^{\infty}\frac{\gamma^n}{n!}n(\hat{a}^\dagger)^{n-1}|0\rangle\\ &= \gamma C\sum_{n=1}^{\infty}\frac{\gamma^{n-1}}{(n-1)!}(\hat{a}^\dagger)^{n-1}|0\rangle = \gamma|\Phi_\gamma\rangle.\end{aligned} \tag{3.94}$$

To find the normalization constant, we need to impose $\langle\Phi_\gamma|\Phi_\gamma\rangle = 1$. Bearing in mind Eq. (3.72), we have

$$|\Phi_\gamma\rangle = C\sum_{n=0}^{\infty}\frac{\gamma^n}{n!}(\hat{a}^\dagger)^n|0\rangle = C\sum_{n=0}^{\infty}\frac{\gamma^n}{\sqrt{n!}}|n\rangle \tag{3.95}$$

Hence

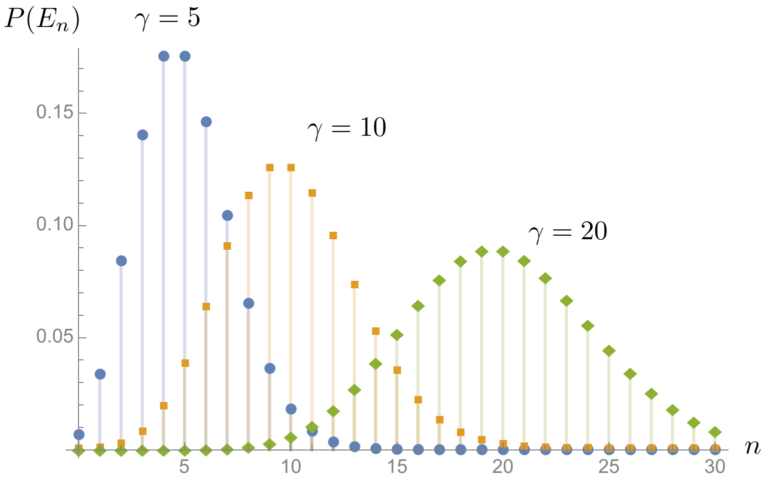


Fig. 3.3 Poisson distribution for various values of γ

$$\langle \Phi_\gamma | \Phi_\gamma \rangle = |C|^2 \sum_{n,n'=0}^{\infty} \frac{(\gamma^*)^n \gamma^{n'}}{\sqrt{n! n'!}} \underbrace{\langle n | n' \rangle}_{\delta_{n,n'}} = |C|^2 \sum_{n=0}^{\infty} \frac{|\gamma|^{2n}}{n!} = |C|^2 e^{|\gamma|^2} \tag{3.96}$$

We conclude that $|C| = e^{-\frac{|\gamma|^2}{2}}$, and thus the state $|\Phi_\gamma\rangle$ is given by

$$\boxed{|\Phi_\gamma\rangle = e^{-\frac{|\gamma|^2}{2}} e^{\gamma \hat{a}^\dagger} |0\rangle} \tag{3.97}$$

Varying γ in the domain of complex numbers, these states are called **coherent states**.

If the particle is in the coherent state $|\Phi_\gamma\rangle$, the probability of measuring energy $E_n = \hbar\omega(n + \frac{1}{2})$ is

$$P(E_n) = |\langle n | \Phi_\gamma \rangle|^2 = e^{-|\gamma|^2} \frac{|\gamma|^{2n}}{n!}. \tag{3.98}$$

This probability distribution is known as the **Poisson distribution**. In Fig. 3.3, the values of $P(E_n)$, with $n = 0, \ldots, 30$, are shown for three different values of γ, and as can be seen, it is highest for $n \sim \gamma$.

Let us now consider the average value of the position operator. We rewrite Eq. (3.58) using the definition of x_0 in Eq. (3.81)

$$\hat{x} = \frac{x_0}{\sqrt{2}} (\hat{a} + \hat{a}^\dagger). \tag{3.99}$$

We have

$$\begin{aligned}\langle\Phi_\gamma|\hat{x}|\Phi_\gamma\rangle = \frac{x_0}{\sqrt{2}}\left(\langle\Phi_\gamma|\hat{a}|\Phi_\gamma\rangle + \langle\Phi_\gamma|\hat{a}^\dagger|\Phi_\gamma\rangle\right) &= \frac{x_0}{\sqrt{2}}\,2\,\mathrm{Re}[\langle\Phi_\gamma|\hat{a}|\Phi_\gamma\rangle]\\ &= \sqrt{2}\,x_0\,\mathrm{Re}[\gamma] \qquad (3.100)\end{aligned}$$

So, the average value of the position operator is not zero if the particle is described by a coherent state. Let us study how the coherent state evolves in time. Without loss of generality, assume that $|\Phi_\gamma\rangle$ describes the particle at time $t = 0$, so $|\Psi(0)\rangle = |\Phi_\gamma\rangle$, and denote by $|\Psi(t)\rangle$ the ket describing the particle at time t. Since the Hamiltonian is time-independent, Eq. (1.152) holds, and therefore

$$\begin{aligned}|\Psi(t)\rangle = e^{-\frac{\mathrm{i}\hat{H}t}{\hbar}}|\Phi_\gamma\rangle = e^{-\frac{|\gamma|^2}{2}}\sum_{n=0}^{\infty}\frac{\gamma^n}{\sqrt{n!}}e^{-\frac{\mathrm{i}\hat{H}t}{\hbar}}|n\rangle = e^{-\frac{|\gamma|^2}{2}}\sum_{n=0}^{\infty}\frac{\gamma^n}{\sqrt{n!}}e^{-\mathrm{i}(n+\frac{1}{2})\omega t}|n\rangle\\ = e^{-\frac{\mathrm{i}\omega t}{2}}e^{-\frac{|\gamma|^2}{2}}\sum_{n=0}^{\infty}\frac{(\gamma e^{-\mathrm{i}\omega t})^n}{\sqrt{n!}}|n\rangle = e^{-\frac{\mathrm{i}\omega t}{2}}|\Phi_{\gamma e^{-\mathrm{i}\omega t}}\rangle. \qquad (3.101)\end{aligned}$$

This result is extremely interesting. It tells us that if the initial state is a coherent state described by the complex number γ, then the state at time t is still a coherent state but it is described by the complex number $\gamma e^{-\mathrm{i}\omega t}$. Using Eq. (3.100), we conclude that the average value of the position operator at time t is given by

$$\langle\Psi(t)|\hat{x}|\Psi(t)\rangle = \langle\Phi_{\gamma e^{-\mathrm{i}\omega t}}|\hat{x}|\Phi_{\gamma e^{-\mathrm{i}\omega t}}\rangle = \sqrt{2}\,x_0\,\mathrm{Re}[\gamma e^{-\mathrm{i}\omega t}] \qquad (3.102)$$

Writing the complex number γ in terms of its modulus and phase, $\gamma = |\gamma|e^{\mathrm{i}\phi}$, we find

$$\boxed{\langle\Psi(t)|\hat{x}|\Psi(t)\rangle = \sqrt{2}\,x_0|\gamma|\cos(\omega t - \phi)} \qquad (3.103)$$

The average position behaves as a classical trajectory! The same applies to the average value of momentum. To demonstrate this, we can use Ehrenfest's theorem

$$\frac{d}{dt}\langle\Psi(t)|\hat{x}|\Psi(t)\rangle = \frac{d}{dt}\langle\Phi_\gamma|e^{\mathrm{i}\frac{\hat{H}t}{\hbar}}\hat{x}e^{-\mathrm{i}\frac{\hat{H}t}{\hbar}}|\Phi_\gamma\rangle = \frac{\mathrm{i}}{\hbar}\langle\Psi(t)|[\hat{H},\hat{x}]|\Psi(t)\rangle. \qquad (3.104)$$

We have

$$[\hat{H},\hat{x}] = \left[\frac{\hat{p}^2}{2m} + V(\hat{x}),\hat{x}\right] = \frac{1}{2m}[\hat{p}^2,\hat{x}] = -\frac{\mathrm{i}\hbar}{m}\hat{p} \qquad (3.105)$$

and hence

$$\frac{d}{dt}\langle\Psi(t)|\hat{x}|\Psi(t)\rangle = \frac{1}{m}\langle\Psi(t)|\hat{p}|\Psi(t)\rangle \qquad (3.106)$$

just as in the classical case. Note that to obtain Eq. (3.106), we have not assumed that the initial state was a coherent state, nor have we assumed that the potential V was the potential of the harmonic oscillator. In fact, regardless of the initial state $|\Psi\rangle$ and the potential V, Ehrenfest's theorem implies that

$$\boxed{\frac{d}{dt}\langle\Psi(t)|\hat{x}|\Psi(t)\rangle = \frac{1}{m}\langle\Psi(t)|\hat{p}|\Psi(t)\rangle} \tag{3.107}$$

To complete the characterization of coherent states, we now calculate the wavefunction $\Phi_\gamma(x) = \langle x|\Phi_\gamma\rangle$ associated with the coherent state. Multiply Eq. (3.90) by the bra $\langle x|$ and write the operator $\hat{a}$ as the dagger of Eq. (3.84), which means

$$\hat{a} = \frac{1}{\sqrt{2}}\left(\frac{\hat{x}}{x_0} + \mathrm{i}\frac{x_0\hat{p}}{\hbar}\right). \tag{3.108}$$

Introducing the dimensionless variable $\bar{x} = x/x_0$ as before, we have

$$\langle x|\hat{a}|\Phi_\gamma\rangle = \frac{1}{\sqrt{2}}\left(\bar{x} + \frac{d}{d\bar{x}}\right)\Phi_\gamma(x) = \gamma\Phi_\gamma(x). \tag{3.109}$$

It's easy to verify that this equation is solved by

$$\Phi_\gamma(x) = Ce^{-\frac{\bar{x}^2}{2}+\sqrt{2}\bar{x}\gamma} \tag{3.110}$$

with C the normalization constant. Let us split γ into a real part γ_1 and an imaginary part γ_2: $\gamma = \gamma_1 + \mathrm{i}\gamma_2$. Then, we can write $\Phi_\gamma(x)$ as

$$\Phi_\gamma(x) = Ce^{\mathrm{i}\sqrt{2}\bar{x}\gamma_2}e^{\gamma_1^2}e^{-\frac{(\bar{x}-\sqrt{2}\gamma_1)^2}{2}}. \tag{3.111}$$

As usual, we fix the constant C by requiring that $\langle\Phi_\gamma|\Phi_\gamma\rangle = 1$. We find

$$\begin{aligned}1 = \langle\Phi_\gamma|\Phi_\gamma\rangle &= \int dx\langle\Phi_\gamma|x\rangle\langle x|\Phi_\gamma\rangle = \int dx|\Phi_\gamma(x)|^2\\ &= |C|^2e^{2\gamma_1^2}x_0\int d\bar{x}\ e^{-(\bar{x}-\sqrt{2}\gamma_1)^2}\\ &= |C|^2e^{2\gamma_1^2}\sqrt{\pi x_0^2},\end{aligned} \tag{3.112}$$

from which it follows that $C = e^{-\gamma_1^2}/(\pi x_0^2)^{\frac{1}{4}}$. In conclusion,

$$\boxed{\Phi_\gamma(x) = \frac{1}{(\pi x_0^2)^{\frac{1}{4}}}\ e^{\mathrm{i}\sqrt{2}\bar{x}\gamma_2}e^{-\frac{(\bar{x}-\sqrt{2}\gamma_1)^2}{2}}} \tag{3.113}$$

Therefore, the probability density $P(x) = |\Phi_\gamma(x)|^2$ is a Gaussian with a width of x_0 centered at $\sqrt{2}x_0\gamma_1$. The probability density at time t is obtained by simply replacing $\gamma \to \gamma e^{-\mathrm{i}\omega t} = |\gamma|e^{-\mathrm{i}\omega t+\mathrm{i}\phi} = |\gamma|\cos(\omega t - \phi) - \mathrm{i}|\gamma|\sin(\omega t - \phi)$, as seen in Eq. (3.101). So, at time t, we have $\gamma_1 = |\gamma|\cos(\omega t - \phi)$ and $\gamma_2 = -|\gamma|\sin(\omega t - \phi)$. This means that the probability density at time t remains a Gaussian with a width of x_0, but the center of the Gaussian shifts in time as $\sqrt{2}x_0|\gamma|\cos(\omega t - \phi)$. As expected, the center of the Gaussian coincides with the mean value of the position operator, as shown in Eq. (3.103). Since the probability density changes over time, we also expect a nonzero current density $J(x, t)$. In fact, $\Psi_\gamma(x)$ is a complex function, and it is easy to verify that $J(x, t)$ is nonzero, and that the continuity equation is satisfied.

3.6 Exercises

1. Consider a quantum particle of mass m in one dimension subject to a step potential $V(x) = V\theta(x)$.

   i. Write the eigenfunctions $\varphi_E(x)$ of energy $0 \leq E \leq V$ in regions $x \leq 0$ and $x \geq 0$.

   ii. Suppose that at time $t = 0$ the particle is described by the wave function $\psi(x) = \frac{1}{\sqrt{2}}[\varphi_{E_1}(x) + \varphi_{E_2}(x)]$ with energies $E_1 = V$ and $E_2 = V/2$ (so $\psi(x)$ is a linear combination of two eigenfunctions of the previous point). Write the wave function $\psi(x, t)$ at time t in regions $x \leq 0$ and $x \geq 0$.

   iii. The probability current at the generic time t is given by $J(x, t) = \frac{\hbar}{m}\mathrm{Im}[\psi^* (x, t)\frac{d}{dx}\psi(x, t)]$. Calculate $J(0, t)$ (i.e. the value of the current at $x = 0$). Express the result in terms of m e V.

   Solution *For energies E below V the generic wave function is given by*

   $$\varphi_E(x) = \begin{cases} e^{\mathrm{i}kx} + D^{-\mathrm{i}kx} & x \leq 0 \\ Te^{-qx} & x \geq 0 \end{cases}$$

   with $k^2 = 2mE/\hbar^2$ and $q^2 = 2m(V - E)/\hbar^2$. *By imposing that the wavefunction is continuous and with continuous derivative is found* $R = -\frac{q+\mathrm{i}k}{q-\mathrm{i}k}$ and $T = -\frac{2\mathrm{i}k}{q-\mathrm{i}k}$.

   ii. *For* $E = E_1 = V$ *we find* $q_1 = 0$ *and* $k_1^2 = 2mV/\hbar^2$, *and hence* $R_1 = 1$ *and* $T_1 = 2$. For $E = E_2 = V/2$ we find $k_2^2 = q_2^2 = mV/\hbar^2$ so $R_2 = -\frac{(1+\mathrm{i})}{1-\mathrm{i}}$ and $T_2 = -\frac{2\mathrm{i}}{1-\mathrm{i}}$. *The wavefunction at time t is therefore*

   $$\begin{aligned} \psi(x, t) &= \frac{1}{\sqrt{2}}\left(\psi_{E_1}(x)e^{-\frac{\mathrm{i}E_1 t}{\hbar}} + \psi_{E_2}(x)e^{-\frac{\mathrm{i}E_2 t}{\hbar}}\right) \\ &= \begin{cases} \frac{1}{\sqrt{2}}\left(e^{\mathrm{i}k_1x} + e^{-\mathrm{i}k_1x}\right)e^{\frac{-\mathrm{i}Vt}{\hbar}} + \frac{1}{\sqrt{2}}\left(e^{\mathrm{i}k_2x} - \frac{(1+\mathrm{i})}{1-\mathrm{i}}e^{-\mathrm{i}k_2x}\right)e^{-\frac{\mathrm{i}Vt}{2\hbar}} & x \leq 0 \\ \frac{1}{\sqrt{2}}2e^{\frac{-\mathrm{i}Vt}{\hbar}} - \frac{1}{\sqrt{2}}\frac{2\mathrm{i}}{1-\mathrm{i}}e^{-q_2x}e^{-\frac{\mathrm{i}Vt}{2\hbar}} & x \geq 0 \end{cases} \end{aligned}$$

   iii. *For* $x = 0$ *we can use the expression of* $\psi(x, t)$ *valid for* $x \geq 0$. *We then have* $\frac{d}{dx}\psi(x, t) = q_2\frac{\sqrt{2}\mathrm{i}}{1-\mathrm{i}}e^{-q_2x}e^{-\frac{\mathrm{i}Vt}{2\hbar}}$. So

$$j(0,t) = \frac{\hbar}{m}\mathrm{Im}\left[\sqrt{2}e^{\frac{\mathrm{i}Vt}{\hbar}} q_2 \frac{\sqrt{2}\mathrm{i}}{1-\mathrm{i}} e^{-\frac{\mathrm{i}Vt}{2\hbar}}\right] = \frac{\hbar}{m}\sqrt{\frac{mV}{\hbar^2}}\mathrm{Im}\left[(\mathrm{i}-1)e^{\frac{\mathrm{i}Vt}{2\ hbar}}\right]$$
$$= \sqrt{\frac{V}{m}}\left(\cos\frac{Vt}{2\hbar} - \sin\frac{Vt}{2\hbar}\right)$$

2. Let the Hamiltonian for a particle in one dimension be given by $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$ with
$$V(x) = -a\delta(x) + V\theta(x),$$
   with $\theta(x)$ the Heaviside step function which is equal to 1 if $x > 0$ and 0 if $x < 0$.
   i. What are the physical dimemsions of a and V?
   ii. Assuming $a > 0$ determine the number of bound states as $V > 0$ is varied.
   iii. Calculate the current density $J(x)$ for the bound states (if they exist).
   Solution *i. The physical dimensions of a are [Energy][Length] while those of V are [Energy].*
   ii. Since V > 0 *the bound state must have energy E* < 0. *The wave function then has the form*
$$\psi(x) = \begin{cases} Ae^{kx} & x < 0 \\ Be^{-px} & x > 0 \end{cases}$$
   with $k = \sqrt{2m|E|/\hbar^2}$ *and* $p = \sqrt{k^2 + 2mV/\hbar^2}$. *By imposing the continuity condition we find* $A = B$ *and by imposing the discontinuity condition of the first derivative is found* $p + k = 2ma/\hbar^2$. *Expressing p in terms of k and solving for k we find*
$$k = \frac{ma}{\hbar^2} - \frac{V}{2a}.$$
   So we have one bound state for $V < 2ma^2/\hbar^2$ *and zero bound states for* $V > 2ma^2/\hbar^2$.
   Since $\psi(x)$ *is real the current is zero.*
3. A particle of mass m in one dimension is described by the Hamiltonian $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$ where
$$V(x) = \begin{cases} \frac{1}{2}m\omega^2x^2 & x < a \\ V_0 & x > a \end{cases}$$
   It is observed that the ground state wavefunction of the harmonic oscillator $\Psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega x^2}{2\hbar}}$ satisfies $[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)]\Psi_0(x) = \frac{\hbar\omega}{2}\Psi_0(x)$ for $x < a$.
   i. If $V_0 > \frac{\hbar\omega}{2}$ what is the most general function $\psi(x)$ that satisfies $[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)]\psi(x) = \frac{\hbar\omega}{2}\psi(x)$ for $x > a$?
   ii. For which value of $V_0 > \frac{\hbar\omega}{2}$ does an energy eigenstate exist at energy $\hbar\omega/2$?
   iii. If $V_0 < \frac{\hbar\omega}{2}$ what is the most general function $\psi(x)$ that satisfies $[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)]\psi(x) = \frac{\hbar\ w}{2}\psi(x)$ for $x > a$?

iv. In the case $V_0 < \frac{\hbar\omega}{2}$ determine the eigenfunction $\varphi(x)$ such that $[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)]\varphi(x) = \frac{\hbar\omega}{2}\varphi(x)\ \forall x$.

Solution *i. The required function is* $\psi(x) = Ae^{-kx}$ *with* $k = \sqrt{\frac{2m}{\hbar^2}(V_0 - \frac{\hbar\omega}{2})}$
ii. For there to be a bound state of energy $\frac{\hbar\omega}{2}$ *the functions* $\Psi_0(x)$, $\psi(x)$ *and their derivatives* $\Psi_0'(x)$, $\psi'(x)$ *must coincide at* $x = a$. *From* $\Psi_0(a) = \psi(a)$ *we find* $Ae^{-ka} = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega a^2}{2\hbar}}$ *while from* $\Psi_0'(a) = \psi'(a)$ *we find* $-kAe^{-ka} = -\left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{m\omega a}{\hbar} e^{-\frac{m\omega a^2}{2\hbar}}$. *Obtaining A from the first and substituting in second we find the condition* $\frac{m\omega a}{\hbar} = k = \sqrt{\frac{2m}{\hbar^2}(V_0 - \frac{\hbar\omega}{2})}$ *from which the required value is evident* $V_0 = \frac{\hbar\omega}{2} + \frac{1}{2}m\omega^2 a^2$.
iii. The required function is $\psi(x) = Be^{iqx} + Ce^{-iqx}$ *with* $q = \sqrt{\frac{2m}{\hbar^2}(\frac{\hbar\omega}{2} - V_0)}$
iv. Now having two constants B and C there always exists a solution $\varphi(x)$ *of energy* $\frac{\hbar\omega}{2}$. *In fact, it is enough to impose the* $\Psi_0(a) = \psi(a)$ *and* $\Psi_0'(a) = \psi'(a)$ *and the solution is* $\varphi(x) = \varphi_0(x)$ *for* $x < a$ *and* $\varphi(x) = \psi(x)$ *for* $x > a$. *For the constants B and C we easily find*

$$B = C^* = \left(\frac{1}{2} - \frac{m\omega a}{2\mathrm{i}\hbar q}\right)\left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega a^2}{2\hbar}} e^{-\mathrm{i}qa}$$

4. Consider a particle of mass m in one dimension subject to the potential

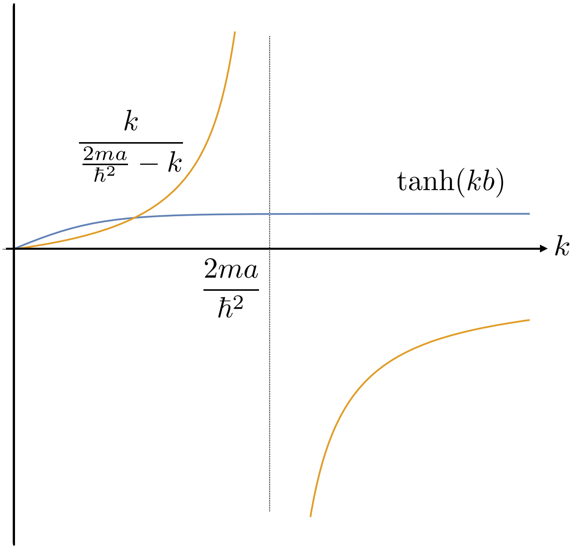
$$V(x) = \begin{cases} \infty & x < 0 \\ -a\delta(x-b) & x > 0 \end{cases}$$

with $a > 0$ and $b > 0$. Once the value of a is fixed, we ask
i. Determine for which values of b there is at least one bound state.
ii. There can be two or more bound states?
Solution *The value of the potential for* $x \to \infty$ *is zero while for* $x \to -\infty$ *is* ∞; *therefore we must look for eigenfunctions of energy less than zero. Given the structure of the potential, the generic eigenfunction of energy E less than zero can be written as*

$$\psi(x) = \begin{cases} 0 & x < 0 \\ Ae^{kx} + Be^{-kx} & 0 < x < b \\ Ce^{-kx} & x > b \end{cases}$$

where $k = \sqrt{\frac{2m|E|}{\hbar^2}} > 0$. *By imposing the continuity condition at* $x = 0$ *we find immediately* $A = -B$. *By imposing the continuity condition in* $x = b$ *we find* $A(e^{2kb} - 1) = C$. *Finally, by imposing the condition on the discontinuity of the first derivative in* $x = b$ *is found* $-Ck - Ak(e^{2kb} + 1) = -\frac{2ma}{\hbar^2}C$. *Substituting in this last equation the value of C obtained previously we obtain*

$$\frac{k}{\frac{2ma}{\hbar^2} - k} = \tanh(kb)$$



As can be seen from the graph, for there to exist a k *such that the two functions can be equal, the first derivative at* $k = 0$ *of the function on the left must be less than the first derivative at* $k = 0$ *of the function on the right side of the equation. This brings us to the condition sought*

$$\frac{d}{dk}\left.\frac{k}{\frac{2ma}{\hbar^2} - k}\right|_{k=0} = \frac{\hbar^2}{2ma} < \frac{d}{dk}\tanh(kb)|_{k=0} = b$$

So if the delta is too close to the barrier there are no bound states. Furthermore, from the graphical solution it is clear that there cannot be more than one bound state.

5. Consider a particle of mass m described by the Hamiltonian of the harmonic oscillator $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$. The particle is in the coherent state $|\Phi_\gamma\rangle = e^{-\frac{|\gamma|^2}{2}} e^{\gamma \hat{a}^\dagger}|0\rangle$, where $|0\rangle$ is the ground state of $\hat{H}$ and the operator $\hat{a}^\dagger = \frac{1}{\sqrt{2}}(\frac{\hat{x}}{x_0} - \mathrm{i}\frac{x_0\hat{p}}{\hbar})$ with $x_0 = \sqrt{\frac{\hbar}{m\omega}}$. In the case where $\gamma = e^{\mathrm{i}\alpha}$ with real α determine
i. The average value $\langle\Phi_\gamma|\hat{x}^2|\Phi_\gamma\rangle$ and establish for which values of α it is maximum
ii. The average value $\langle\Phi_\gamma|\hat{p}^2|\Phi_\gamma\rangle$ and establish for which values of α it is maximum
iii. The product of the variances $\langle\hat{\sigma}_p^2\rangle\langle\hat{\sigma}_x^2\rangle$ and establish for which values of α it is minimum. Then check the Heisenberg uncertainty principle.

Solution *Recall that* $\hat{a}|\Phi_\gamma\rangle = \gamma|\Phi_\gamma\rangle$ *and that* $\langle\Phi_\gamma|\Phi_\gamma\rangle = 1$. *The result of* $\hat{x} = \frac{x_0}{\sqrt{2}}(\hat{a} + \hat{a}^\dagger)$, *is therefore*

$$\langle\Phi_\gamma|\hat{x}^2|\Phi_\gamma\rangle = \frac{x_0^2}{2}\langle\Phi_\gamma|\hat{a}^2 + (\hat{a}^\dagger)^2 + \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a}|\Phi_\gamma\rangle = x_0^2\left[\frac{3}{2} + \cos(2\alpha)\right]$$

Therefore the average value $\langle\Phi_\gamma|\hat{x}^2|\Phi_\gamma\rangle$ *is maximum for* $\alpha = n\pi$ *with n integer. It turns out then* $\hat{p} = \frac{\hbar}{\mathrm{i}\sqrt{2}x_0}(\hat{a} - \hat{a}^\dagger)$. So

$$\langle\Phi_\gamma|\hat{p}^2|\Phi_\gamma\rangle = -\frac{\hbar^2}{2x_0^2}\langle\Phi_\gamma|\hat{a}^2 + (\hat{a}^\dagger)^2 - \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a}|\Phi_\gamma\rangle = \frac{\hbar^2}{x_0^2}\left[\frac{3}{2} - \cos(2\alpha)\right]$$

Therefore the average value $\langle\Phi_\gamma|\hat{p}^2|\Phi_\gamma\rangle$ *is maximum for* $\alpha = n\pi + \pi/2$ *with n integer. Being then* $\langle\Phi_\gamma|\hat{x}|\Phi_\gamma\rangle = \sqrt{2}x_0\cos(\alpha)$ and $\langle\Phi_\gamma|\hat{p}|\Phi_\gamma\rangle = \sqrt{2}\frac{\hbar}{x_0}\sin(\alpha)$ *we have*

$$\begin{aligned}\langle\hat{\sigma}_x^2\rangle &= x_0^2\left[\frac{3}{2} + \cos(2\alpha)\right] - 2x_0^2\cos^2(\alpha) = x_0^2\left[\frac{3}{2} + \cos^2(\alpha) - \sin^2(\alpha) - 2\cos^2(\alpha)\right]\\ &= \frac{x_0^2}{2}\end{aligned}$$

$$\begin{aligned}\langle\hat{\sigma}_p^2\rangle &= \frac{\hbar^2}{x_0^2}\left[\frac{3}{2} - \cos(2\alpha)\right] - 2\frac{\hbar^2}{x_0^2}\sin^2(\alpha) = \frac{\hbar^2}{x_0^2}\left[\frac{3}{2} - \cos^2(\alpha) + \sin^2(\alpha) - 2\sin^2(\alpha)\right]\\ &= \frac{\hbar^2}{2x_0^2}\end{aligned}$$

The requested product $\langle\hat{\sigma}_x^2\rangle\langle\hat{\sigma}_p^2\rangle = \frac{\hbar^2}{4}$ *is independent of* α *and saturates the Heisenberg uncertainty principle.*

6. Consider a particle of mass m in one dimension subject to the potential $V(x) = a\delta(x)$ with $a > 0$.
i. Determine the two degenerate eigenfunctions $\psi_1(x)$ and $\psi_2(x)$ of energy $E = \frac{ma^2}{2\hbar^2} > 0$.
ii. Consider the wave function $\varphi(x) = \frac{1}{\sqrt{2}}[\psi_1(x) + e^{\mathrm{i}\beta}\psi_2(x)]$. Calculate the phase β so that the current $J(x) = \frac{\hbar}{m}\mathrm{Im}[\varphi^*(x)\frac{d}{dx}\varphi(x)]$ is equal to $\frac{a}{2\hbar}$.
Solution *i. The degenerate eigenfunctions of energy* $E = \frac{\hbar^2k^2}{2m} > 0$ *are given by*

$$\psi_1(x) = \begin{cases} e^{\mathrm{i}kx} + D^{-\mathrm{i}kx} & x < 0 \\ Te^{\mathrm{i}kx} & x > 0 \end{cases} \qquad \psi_2(x) = \begin{cases} Te^{-\mathrm{i}kx} & x < 0 \\ e^{-\mathrm{i}kx} + D^{\mathrm{i}kx} & x > 0 \end{cases}$$

with $R = \frac{1}{\mathrm{i}\gamma - 1}$, $T = \frac{1}{1 + \mathrm{i}/\gamma}$ and $\gamma = \frac{\hbar^2k}{ma}$. *It's easy to verify that* $|R|^2 + |T|^2 = 1$. *Having the energy to be* $E = \frac{ma^2}{2\hbar^2}$ gives $k = \frac{ma}{\hbar^2}$ and so $\gamma = 1$.

ii. Since $\varphi(x)$ is a linear combination of degenerate eigenfunctions the probability density is independent of time and therefore the current must be independent of position. Let's calculate then the current for $x > 0$:

$$J(x) = \frac{\hbar}{2m}\mathrm{Im}\left[ik\left(T^* e^{-ikx} + e^{-i\beta}(e^{ikx} + R^* e^{-ikx})\right)\left(Te^{ikx} + e^{i\beta}(-e^{-ikx} + D^{ikx})\right)\right]$$
$$= \frac{\hbar k}{m}\mathrm{Re}[e^{i\beta}T^* R)] = \frac{a}{2\hbar}\sin\beta. \tag{3.114}$$

Therefore $\beta = \pi/2$ so that $J(x) = \frac{a}{2\hbar}$.

7. Consider a particle of mass m in one dimension subject to the potential

$$V(x) = \begin{cases} \infty & \text{se } |x| > L/2 \\ \frac{2\hbar^2}{ma}\delta(x) & \text{if } |x| < L/2 \end{cases}$$

Since the potential is even, the eigenfunctions are either even or odd and in the range $(-L/2, L/2)$ they have the form

$$\text{ODD}: \quad \psi(x) = A\begin{cases} \sin k(x + L/2)\ , & x < 0 \\ \sin k(x - L/2)\ , & x > 0 \end{cases}$$

$$\text{EVEN}: \quad \psi(x) = A\begin{cases} \sin k(x + L/2) & , \quad x < 0 \\ -\sin k(x - L/2)\ , & x > 0 \end{cases}$$

Determine the possible values of k in the even and odd cases.

Solution *In the case of odd parity, the continuity condition at $x = 0$ is satisfied for $k = 2n\pi/L$, and for such values of k, the discontinuity condition of the first derivative is automatically satisfied. A possible choice for n to obtain independent eigenfunctions is $n = 1, 2, 3, \ldots$*

In the case of even parity, the continuity condition at $x = 0$ is always satisfied. However, the condition of discontinuity of the first derivative leads to

$$\tan\frac{kL}{2} = -\frac{ka}{2}$$

In this case, independent eigenfunctions are obtained, for example, by taking all positive solutions of the above equation for k.

8. Consider a particle of mass m in one dimension described by the wave function $\Psi(x)$. Knowing that

(1) at $x = 0$ the wave function is real and positive

(2) the probability density $P(x)$ and the probability current $J(x)$ are given by

$$P(x) = e^{-|x/L|}\sqrt{1 + (x/L)^2}, \qquad J(x) = \frac{\hbar}{m}\frac{1}{L}\frac{e^{-|x/L|}}{\sqrt{1 + (x/L)^2}}$$

i. Determine the wave function. (Hint: Write $\Psi(x) = \rho(x)e^{i\theta(x)}$ with ρ and θ real functions. Remember also that $\frac{d}{dx}\text{atan}(x) = \frac{1}{1+x^2}$)
ii. For which values of x is the wave function purely imaginary?
Solution *i. Writing the wavefunction as in the hint is found* $P(x) = \rho(x)^2$ and $J(x) = \frac{\hbar}{m}\rho(x)^2\frac{d\theta(x)}{dx}$. *We therefore have* $\rho(x) = \pm e^{-\frac{1}{2}|x/L|}(1 + (x/L)^2)^{\frac{1}{4}}$. *To determine the sign of* ρ *we observe that at* $x = 0$ *the wave function is real and positive. Choosing* $\theta(0) = 0$ *the sign of* ρ *must be* $+$. *The function* $\theta(x)$ *satisfies*

$$\frac{d\theta(x)}{dx} = \frac{m}{\hbar}\frac{J(x)}{P(x)} = \frac{1}{L}\frac{1}{1 + (x/L)^2}$$

Integrating both members and remembering that we chose $\theta(0) = 0$ *we find* $\theta(x) = \text{atan}(x/L)$.
ii. Using the previously determined $\theta(x)$ *function the wavefunction is purely imaginary only for* $x \to \pm\infty$.

9. Consider a particle of mass m in one dimension subject to the potential of two infinite wells of the same width a and distant from each other $2b$, therefore

$$V(x) = \begin{cases} 0 & \text{if} \quad b < |x| < b + a \\ \infty & \text{otherwise} \end{cases}$$

i. Determine the normalized eigenfunctions and eigenvalues of the Hamiltonian
ii. Determine the degeneracy of the eigenvalues
iii. It is possible to construct an eigenfunction of the Hamiltonian with eigenvalue $\frac{\hbar^2\pi^2}{2ma^2}$ such that the probability of finding the particle in the right well is 1/3? If so, determine the eigenfunction, otherwise motivate why it's not possible.
Solution *i. The eigenvalues* E_n *of the Hamiltonian are the same as those of a single well with infinite walls since the eigenfunctions are those of the single well on the right, let's denote them by* $\varphi_n^{(+)}(x)$, *or of the single well on the left, let's indicate them with* $\varphi_n^{(-)}(x)$. *So* $E_n = \frac{\hbar^2 n^2\pi^2}{2ma^2}$ *with* $n = 1, 2, , \ldots$ *and*

$$\varphi_n^{(+)}(x) = \begin{cases} \sqrt{\frac{2}{a}}\sin\frac{n\pi(x-b)}{a} & b < x < b + a \\ 0 & \text{otherwise} \end{cases}$$

$$\varphi_n^{(-)}(x) = \begin{cases} \sqrt{\frac{2}{a}}\sin\frac{n\pi(x+b)}{a} & -b > x > -b - a \\ 0 & \text{otherwise} \end{cases}$$

ii. From point i. it follows that the degeneracy of each eigenvalue E_n *is equal to 2.*
iii. *The answer is yes. In fact, any linear combination of eigenfunctions with* $n = 1$, *i.e.* $\psi(x) = \alpha\varphi_1^{(+)}(x) + \beta\varphi_1^{(-)}(x)$ *has energy* $E_1 = \frac{\hbar^2\pi^2}{2ma^2}$. *If the particle*

is described by the wavefunction $\psi(x)$ the probability of finding it in the right well is equal to

$$P = \int_b^{b+a} dx|\psi(x)|^2 = |\alpha|^2 \int_b^{b+a} dx|\varphi_1^{(+)}(x)|^2 = |\alpha|^2.$$

It is then enough to choose α such that $|\alpha| = 1/3$.

10. A particle of mass m in one dimension is subject to the potential $V(x) = a\delta(x)$.
i. Determine the two orthonormal eigenfunctions $\varphi_1(x)$ e $\varphi_2(x)$ of energy $E > 0$
ii. Suppose the particle is described by the wave function $\psi(x) = \frac{1}{\sqrt{2}}\big(\varphi_1(x) + e^{\mathrm{i}\theta}\varphi_2(x)\big)$ where $\varphi_1(x)$ e $\varphi_2(x)$ both have energy $E = \frac{ma^2}{2\hbar^2}$. Calculate the current $J(x) = \frac{\hbar}{m}\,\mathrm{Im}[\psi^*(x)\frac{d}{dx}\psi(x)]$ and express it in terms of a and θ.
Solution *i. The two normalized eigenfunctions of energy E are*

$$\varphi_1(x) = \begin{cases} e^{\mathrm{i}kx} + Re^{-\mathrm{i}kx} & x < 0 \\ Te^{\mathrm{i}kx} & x > 0 \end{cases} \qquad \varphi_2(x) = \begin{cases} Te^{-\mathrm{i}kx} & x < 0 \\ e^{-\mathrm{i}kx} + Re^{\mathrm{i}kx} & x > 0 \end{cases}$$

with $k = \sqrt{2mE/\hbar^2}$ and

$$T = \frac{\hbar^2 k}{\hbar^2 k + \mathrm{i}ma}, \qquad R = \frac{-\mathrm{i}ma}{\hbar^2 k + \mathrm{i}ma}$$

ii. If the energy $E = \frac{ma^2}{2\hbar^2}$ then $\hbar^2 k = ma$. The current is independent of x being the wavefunction$\psi(x)$ an eigenfunction of the Hamiltonian. Evaluating the current for $x > 0$ we find

$$\begin{aligned} J &= \frac{\hbar}{2m}\mathrm{Im}\Big[\Big(T^* e^{-\mathrm{i}kx} + e^{-\mathrm{i}\theta}e^{\mathrm{i}kx} + e^{-\mathrm{i}\theta}R^* e^{-\mathrm{i}kx}\Big)\mathrm{i}k\Big(Te^{\mathrm{i}kx} - e^{\mathrm{i}\theta}e^{-\mathrm{i}kx} + e^{\mathrm{i}\theta}Re^{\mathrm{i}kx}\Big)\Big] \\ &= \frac{\hbar k}{m}\mathrm{Re}(e^{\mathrm{i}\theta}T^* R) = \frac{a}{\hbar}\mathrm{Re}\left(e^{\mathrm{i}\theta}\frac{1}{1-\mathrm{i}}\frac{-\mathrm{i}}{1+\mathrm{i}}\right) = \frac{a}{2\hbar}\sin\theta \end{aligned}$$

11. A particle of mass m in one dimension is subject to the potential

$$V(x) = \begin{cases} \infty & \text{se } |x| > L \\ -a\delta(x) & \text{se } |x| < L \end{cases}$$

with $a > 0$. As a varies, find the number of eigenstates of negative energy.
Solution *In the interval $(-L, L)$ the negative energy eigenfunctions have the form*

$$\Psi(x) = \begin{cases} A[e^{k(x+L)} - e^{-k(x+L)}] & \text{se } x < 0 \\ B[e^{k(x-L)} - e^{-k(x-L)}] & \text{se } x > 0 \end{cases}$$

with k real and positive. This form can be easily deduced imposing that $\Psi(-L) = \Psi(L) = 0$. *From the continuity condition in* $x = 0$ *follows that* $B = -A$; *then imposing the discontinuity condition of the first derivative it follows that*

$$\frac{\hbar^2}{ma}k = \tanh(kL)$$

This equation admits zero solutions (and therefore zero bound states) if $a < \frac{\hbar^2}{mL}$ *and one solution (and therefore only one bound state) if* $a > \frac{\hbar^2}{mL}$.

12. A particle is initially in the ground state of the quantum harmonic oscillator described by the Hamiltonian $\hat{H}_1 = \frac{\hat{p}^2}{2m} + \frac{m\omega^2\hat{x}^2}{2}$. At time $t = 0$ the Hamiltonian suddenly changes and becomes $\hat{H}_2 = \frac{\hat{p}^2}{2m} - a\delta(x)$ with $a > 0$. Indicating with P the probability that at time $t > 0$ a measurement of $\hat{H}_2$ gives a negative result
i. Write P as an integral in which only the ratio $\lambda = \frac{\hbar^2}{max_0}$ appears, being $x_0 = \sqrt{\frac{\hbar}{m\omega}}$ the typical length associated with the harmonic oscillator.
ii. Assuming that λ is small calculate P to the third order in λ.
Solution *i. The initial wavefunction is*

$$\Psi_0(x) = \frac{1}{\pi^{1/4}}\sqrt{\frac{1}{x_0}}e^{-\frac{x^2}{2x_0^2}}, \qquad x_0 = \sqrt{\frac{\hbar}{m\omega}}$$

The Hamiltonian $\hat{H}_2$ *has only one eigenvalue negative* $E_0 = -\frac{ma^2}{2\hbar^2}$, *relative to the unique bound state that has a wavefunction*

$$\Phi_0(x) = \sqrt{\frac{1}{x_\delta}}e^{-\frac{|x|}{x_\delta}}, \qquad x_\delta = \frac{\hbar^2}{ma}.$$

The required probability is therefore given by $P = |c_0|^2$ *with*

$$c_0 = \int_{-\infty}^{\infty} dx\, \Phi_0^*(x)\Psi_0(x) = \frac{1}{\pi^{1/4}}\sqrt{\frac{1}{x_0}}\sqrt{\frac{1}{x_\delta}}\int_{-\infty}^{\infty} dx\, e^{-\frac{|x|}{x_\delta}}e^{-\frac{x^2}{2x_0^2}}$$

$$= \frac{1}{\pi^{1/4}}\sqrt{\lambda}\int_{-\infty}^{\infty} dz e^{-|z|-\frac{1}{2}\lambda^2 z^2}$$

ii. Expanding the integral to second order in λ *we find*

$$c_0 \approx \frac{1}{\pi^{1/4}}\sqrt{\lambda}\int_{-\infty}^{\infty} dz e^{-|z|}(1 - \frac{\lambda^2 z^2}{2}) = \frac{2}{\pi^{1/4}}\sqrt{\lambda}(1 - \lambda^2)$$

Therefore the sought probability to third order in λ *is to be*

$$P = |c_0|^2 = \frac{4}{\sqrt{\pi}}(\lambda - 2\lambda^3)$$

13. A quantum particle of mass m in one spatial dimension is subject to potential

$$V(x) = \begin{cases} 0 & \text{per} \quad L/2 < x < L/2 \\ \infty & \text{otherwise} \end{cases}$$

Determine the wavefunction $\psi(x)$ that describes the particle knowing that:
1. An energy measurement will always give a result less than $\frac{5\pi^2\hbar^2}{2mL^2}$
2. The probability that the particle is in the ground state is $1/3$
3. The average of the particle's momentum is $\langle p\rangle = \frac{16\hbar}{9L}$
4. The square modulus of the wavefunction at the point $x = L/4$ is $|\psi(L/4)|^2 = \frac{5+2\sqrt{2}}{3L}$.

Solution *From information 1 we know that the state is a linear combination of* $\phi_1(x)$ and $\phi_2(x)$, *which we can write as* $\psi(x) = a\phi_1(x) + be^{\mathrm{i}\alpha}\phi_2(x)$. *The unknowns a and b are real and positive, while* $0 < \alpha < 2\pi$. *From information 2 we immediately find that* $a = \sqrt{\frac{1}{3}}$ while $b = \sqrt{\frac{2}{3}}$. *To determine* α *we use information 3 and 4. In particular it is found that*

$$\begin{aligned}\langle p\rangle &= \int_{-L/2}^{L/2} dx \left[\sqrt{\frac{1}{3}}\phi_1(x) + e^{-\mathrm{i}\alpha}\sqrt{\frac{2}{3}}\phi_2(x)\right]\left(-\mathrm{i}\hbar\frac{d}{dx}\right)\left[\sqrt{\frac{1}{3}}\phi_1(x) + e^{\mathrm{i}\alpha}\sqrt{\frac{2}{3}}\phi_2(x)\right] \\ &= -\mathrm{i}\hbar\frac{2\sqrt{2}}{3L}\left[e^{\mathrm{i}\alpha}2\int_{-\pi/2}^{\pi/2} dz\cos(z)\cos(2z) - e^{-\mathrm{i}\alpha}\int_{-\pi/2}^{\pi/2} dz\sin(z)\sin(2z)\right] \\ &= \frac{16\sqrt{2}\hbar}{9L}\sin\alpha \\ &= \frac{16\hbar}{9L}\end{aligned}$$

from which it can be deduced that $\sin\alpha = \frac{\sqrt{2}}{2}$. *Using information 4 we find that*

$$|\psi(L/4)|^2 = \left|\sqrt{\frac{1}{3}}\phi_1(L/4) + e^{\mathrm{i}\alpha}\sqrt{\frac{2}{3}}\phi_2(L/4)\right|^2 = \frac{5+4\cos\alpha}{3L} = \frac{5+2\sqrt{2}}{3L}$$

from which it can be deduced that $\cos\alpha = \frac{\sqrt{2}}{2}$. *Putting together the last two pieces of information we conclude that* $\alpha = \pi/4$.

14. The Hamiltonian of a particle of mass m in one dimension is given by $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$, where $V(\hat{x}) = -a\delta(\hat{x}) + a\delta(\hat{x} - L)$ and where a and L are positive. Determine the number of bound states of the system.

Solution *The particle is described by the unknown wavefunction as:*

$$\psi(x) = \begin{cases} Ae^{kx}, & x < 0 \\ Be^{-kx} + Ce^{kx}, & 0 < x < L \\ De^{-kx}, & x > L \end{cases} \tag{3.115}$$

where A, B, C, D and k are constants to be determined. The positive constant k is linked to the energy $E < 0$ of the bound states through the relation $k = \sqrt{2m|E|}/\hbar$. By imposing the continuity of the wave function in $x = 0$ and $x = L$ and the discontinuity of its derivative at the same points in virtue of the potentials $\delta(x)$ and $\delta(x - L)$ we obtain the system of equations

$$\begin{aligned} A - B - C &= 0 \\ Be^{-kL} + Ce^{kL} - De^{-kL} &= 0 \\ \left(\frac{2ma}{\hbar^2} - k\right) A - kB + kC &= 0 \\ kBe^{-kL} - kCe^{kL} - De^{-kL}\left(\frac{2ma}{\hbar^2} + k\right) &= 0 \end{aligned}$$

The value of k that determines the energy of the bound states is found requiring that the system admits a solution. The equation thus obtained is:

$$\left(1 - e^{-2kL}\right) = \frac{\hbar^4 k^2}{m^2 a^2}, \tag{3.116}$$

which admits a unique solution other than $k = 0$ for every $a > 0$ ed $L > 0$. Therefore there is a unique bound state.

15. Consider a one-dimensional quantum harmonic oscillator of mass m e frequency ω described by the Hamiltonian $\hat{H}$ with autokets $|n\rangle$. At time $t = 0$ the system is in the unknown state $|\psi\rangle$.

Determine $|\psi\rangle$ knowing that:

(a) An energy measurement will always give a result less than $3\hbar\omega$,
(b) At time $t = \frac{\pi}{5\omega}$ we have $\langle 3|\hat{a}^\dagger|\psi(t)\rangle = \sqrt{\frac{3}{2}}$,
(c) $\langle\psi|\hat{a}^\dagger\hat{a}|\psi\rangle = 1$.

Solution *From information 1 we know that the state is a combination linear of $|0\rangle, |1\rangle, |2\rangle$. Without losing generality we can write it as*

$$|\psi\rangle = \frac{|0\rangle + \alpha_1|1\rangle + \alpha_2|2\rangle}{\sqrt{1 + |\alpha_1|^2 + |\alpha_2|^2}}$$

with α_1, α_2 complex constants to determine.

From information 2 we obtain that

$$\begin{aligned}\langle 3|\hat{a}^\dagger|\psi(t)\rangle &= \frac{\langle 3|\hat{a}^\dagger\left(|0\rangle e^{-\mathrm{i}E_0t/\hbar} + \alpha_1|1\rangle e^{-\mathrm{i}E_1t/\hbar} + \alpha_2|2\rangle e^{-\mathrm{i}E_2t/\hbar}\right)}{\sqrt{1+|\alpha_1|^2+|\alpha_2|^2}}\\ &= \frac{\sqrt{3}\alpha_2 e^{-\mathrm{i}\frac{5}{2}\omega t}}{\sqrt{1+|\alpha_1|^2+|\alpha_2|^2}} = \frac{-\mathrm{i}\sqrt{3}\alpha_2}{\sqrt{1+|\alpha_1|^2+|\alpha_2|^2}} = \sqrt{\frac{3}{2}}\end{aligned}$$

from which it follows

$$\frac{\alpha_2}{\sqrt{1+|\alpha_1|^2+|\alpha_2|^2}} = \frac{\mathrm{i}}{\sqrt{2}}.$$

Finally, from information 3 we deduce that

$$\langle\psi|\hat{a}^\dagger\hat{a}|\psi\rangle = \frac{|\alpha_1|^2+2|\alpha_2|^2}{1+|\alpha_1|^2+|\alpha_2|^2} = 1$$

From these last two results we can conclude that it must be $\alpha_1 = 0$ *and* $\alpha_2 = \mathrm{i}$. *The sought state is therefore*

$$|\psi\rangle = \frac{|0\rangle + \mathrm{i}|2\rangle}{\sqrt{2}}$$

16. Consider a particle of mass m in one dimension subject to the harmonic potential $V(x) = \frac{1}{2}m\omega^2x^2$. At time $t = 0$ the particle is described by the ket

$$|\Psi\rangle = C\big(|\Phi_\gamma\rangle + |\Phi_{\gamma'}\rangle\big)$$

where $|\Phi_\gamma\rangle$ and $|\Phi_{\gamma'}\rangle$ are two coherent states with $\gamma = \mathrm{i}$ and $\gamma' = -\mathrm{i}$.
i. Determine the normalization constant C
ii. Calculate the average value of the position operator at time t e comment the result in terms of the wavefunction $\Psi(x) = \langle x|\Psi\rangle$
Solution *i. A generic coherent state can be written as* $|\Phi_\gamma\rangle = e^{-|\gamma|^2/2}\sum_{n=0}^{\infty}\frac{\gamma^n}{\sqrt{n!}}|n\rangle$. *Since* $\gamma = \mathrm{i}$ *and* $\gamma' = -\mathrm{i}$ *we have*

$$|\Phi_\gamma\rangle = e^{-1/2}\sum_{n=0}^{\infty}\frac{\mathrm{i}^n}{\sqrt{n!}}|n\rangle, \qquad |\Phi_{\gamma'}\rangle = e^{-1/2}\sum_{n=0}^{\infty}\frac{(-\mathrm{i})^n}{\sqrt{n!}}|n\rangle.$$

Therefore

$$\begin{aligned}\langle\Psi|\Psi\rangle &= |C|^2\Big(2 + \langle\Phi_\gamma|\Phi_{\gamma'}\rangle + \langle\Phi_{\gamma'}|\Phi_\gamma\rangle\Big) = |C|^2\Big(2 + 2\frac{1}{e}\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}\Big)\\ &= |C|^2 2\frac{1+e^2}{e^2}\\ &\Rightarrow \quad C = \frac{e}{\sqrt{2(1+e^2)}}\end{aligned}$$

ii. The ket evolved at time t is $|\Psi(t)\rangle = Ce^{-\mathrm{i}\omega t/2}\Big(|\Phi_{\gamma e^{-\mathrm{i}\omega t}}\rangle + |\Phi_{\gamma' e^{-\mathrm{i}\omega t}}\rangle\Big)$. Therefore set as always $x_0 = \sqrt{\hbar/(m\omega)}$

$$\begin{aligned}\langle\Psi(t)|\hat{x}|\Psi(t)\rangle = \frac{e^2}{2(1+e^2)}\Big\{&\sqrt{2}x_0\mathrm{Re}[\mathrm{i}e^{-\mathrm{i}\omega t}] + \sqrt{2}x_0\mathrm{Re}[-\mathrm{i}e^{-\mathrm{i}\omega t}]\\ &+ \langle\Phi_{\gamma e^{-\mathrm{i}\omega t}}|\hat{x}|\Phi_{\gamma' e^{-\mathrm{i}\omega t}}\rangle + \langle\Phi_{\gamma' e^{-\mathrm{i}\omega t}}|\hat{x}|\Phi_{\gamma e^{-\mathrm{i}\omega t}}\rangle\Big\}\end{aligned}$$

The first two terms in the curly bracket cancel each other out. The third term is the complex conjugate of the fourth term. It turns out

$$\begin{aligned}\langle\Phi_{\gamma e^{-\mathrm{i}\omega t}}|\hat{x}|\Phi_{\gamma' e^{-\mathrm{i}\omega t}}\rangle &= \frac{x_0}{\sqrt{2}}\left(\langle\Phi_{\gamma e^{-\mathrm{i}\omega t}}|\hat{a}|\Phi_{\gamma' e^{-\mathrm{i}\omega t}}\rangle + \langle\Phi_{\gamma' e^{-\mathrm{i}\omega t}}|\hat{a}|\Phi_{\gamma e^{-\mathrm{i}\omega t}}\rangle^*\right)\\ &= \frac{x_0}{\sqrt{2}e^2}\Big(-\mathrm{i}e^{-\mathrm{i}\omega t} - \mathrm{i}e^{\mathrm{i}\omega t}\Big) = -\mathrm{i}\frac{x_0\sqrt{2}}{e^2}\cos\omega t\end{aligned}$$

which is purely imaginary. We conclude that $\langle\Psi(t)|\hat{x}|\Psi(t)\rangle = 0$. This result is a consequence of the fact that the wave function at time t, i.e

$$\Psi(x) = \langle x|\Psi\rangle = \frac{C}{(\pi x_0^2)^{1/4}}\Big(e^{\mathrm{i}\sqrt{2}\bar{x}\sin\omega t}e^{-(\bar{x}-\sqrt{2}\cos\omega t)^2/2} + e^{-\mathrm{i}\sqrt{2}\bar{x}\sin\omega t}e^{-(\bar{x}+\sqrt{2}\cos\omega t)^2/2}\Big)$$

is even for every t.

17. Consider a particle of mass m constrained to move along the z axis. The particle is attached to one end of a spring with elastic constant k and zero rest length, the other end of the spring is instead fixed. Furthermore, the particle is subject to the force of gravity $F = -mg$ directed along the z axis. Choosing $z = 0$ to be the point of the fixed end of the spring we can write the potential energy of the particle as $V(z) = mgz + \frac{1}{2}kz^2$. So the Lagrangian is $\mathcal{L}(z, \dot{z}) = \frac{m}{2}\dot{z}^2 - mgz - \frac{1}{2}kz^2$.
i. Calculate the conjugate momentum $p = \partial\mathcal{L}/\partial\dot{z}$.
ii. Write the Hamiltonian $H(z, p) = p\dot{z} - \mathcal{L}(z, \dot{z})$.
iii. Using the postulates of quantum mechanics to quantize the problem, find eigenkets and eigenvalues of the Hamiltonian.
iv. How much does the spring constant k have to be for the energy of the ground state be zero?
Solution *i. The moment conjugated to z is $p = \frac{\partial\mathcal{L}}{\partial\dot{z}} = m\dot{z}$.*
ii. The Hamiltonian is $H(z, p) = p\dot{z} - \mathcal{L}(z, \dot{z}) = \frac{p^2}{2m} + mgz + \frac{1}{2}kz^2$
iii. Using the postulates of quantum mechanics the Hamiltonian becomes the operator $\hat{H} = \frac{\hat{p}^2}{2m} + mg\hat{z} + \frac{1}{2}k\hat{z}^2$ with $[\hat{z}, \hat{p}] = \mathrm{i}\hbar$. It is convenient to define $\omega = \sqrt{\frac{k}{m}}$e rewrite $\hat{H}$ as $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2(\hat{z} + \frac{g}{\omega^2})^2 - \frac{m}{2}\frac{g^2}{\omega^2}$. Introducing operators $\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}(\hat{z} + \frac{g}{\omega^2}) + \mathrm{i}\frac{hatp}{\sqrt{2m\hbar\omega}}$ and $\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}(\hat{z} + \frac{g}{\omega^2}) - \mathrm{i}\frac{\hat{p}}{\sqrt{2m\hbar\omega}}$ we can rewrite $\hat{H} = \hbar\omega(\hat{a}^\dagger\hat{a} + \frac{1}{2}) - \frac{m}{2}\frac{g^2}{\omega^2}$, where we exploited $[\hat{a}, \hat{a}^\dagger] = 1$. Therefore

if we define the ket $|0\rangle$ *to be the eigenket of* $\hat{a}$ *with zero eigenvalue we have that the eigenkets of the Hamiltonian are* $|n\rangle = \frac{(\hat{a}^\dagger)^n}{\sqrt{n!}}|0\rangle$ *and their energy is* $E_n = \hbar\omega(n+\frac{1}{2}) - \frac{m}{2}\frac{g^2}{\omega^2}$.

iv. For the ground state energy to be zero it must be $E_0 = 0$ *and therefore* $\omega = (\frac{mg^2}{\hbar})^{1/3}$ *from which* $k = m(\frac{mg^2}{\hbar})^{2/3}$.

18. A system is at time $t = 0$ in a state $|\psi\rangle$ which is a linear combination of the ground state $|0\rangle$ and of the first excited state $|1\rangle$ of a one-dimensional quantum harmonic oscillator of Hamiltonian $\hat{H}$, with frequency ω and mass m.

i. Knowing that the average of energy, position and momentum on this state are respectively $\langle E\rangle = \frac{7}{6}\hbar\omega$, $\langle x\rangle = \frac{1}{3}\sqrt{\frac{2\hbar}{m\omega}}$ and $\langle p\rangle = -\frac{1}{3}\sqrt{2m\hbar\omega}$, determine $|\psi\rangle$ in terms of $|0\rangle$ and $|1\rangle$.

ii. For $t > 0$ the state evolves according to the Hamiltonian $\hat{H}$. Determine the probability that at the generic time t the state is found in the coherent state $|\Phi_\gamma\rangle = e^{-\frac{\gamma^2}{2}}e^{\gamma\hat{a}^\dagger}|0\rangle$ with real γ.

iii. Explain why this probability can never be 1.

Solution *i. The generic state* $|\psi\rangle$ *can be written as* $|\psi\rangle = a|0\rangle + be^{i\theta}|1\rangle$ *where a and b are real and positive, e* $-\pi \le \theta < \pi$. *Normalization forces* $a^2 + b^2 = 1$. *From the condition* $\langle E\rangle = \frac{7}{6}\hbar\omega$ *follows immediately* $a^2 + 3b^2 = 7/3$, *which together with the normalization condition gives* $a = \frac{1}{\sqrt{3}}$ *e* $b = \sqrt{\frac{2}{3}}$. *To determine the phase we must use the other two pieces of information. In particular from that on the position we find* $ab\cos\theta = \frac{1}{3}$ *and therefore* $\cos\theta = \frac{1}{\sqrt{2}}$. *The solution gives* $\theta = \pm\pi/4$. *To determine the sign of the phase we must use the information about the momentum, which gives* $ab\sin\theta = -\frac{1}{3}$ *and therefore* $\theta = -\pi/4$.

ii. The state evolved at time t is $|\psi(t)\rangle = \frac{1}{\sqrt{3}}e^{-i\frac{\omega}{2}t}|0\rangle + \sqrt{\frac{2}{3}}e^{-i\pi/4}e^{-i\frac{3\omega}{2}t}|1\rangle$. *The probability* $P_\gamma(t)$ *that the state* $|\psi(t)\rangle$ *is in the coherent state* $|\Phi_\gamma\rangle$ *is given by* $P_\gamma(t) = |\langle\psi(t)|\Phi_\gamma\rangle|^2$, *where*

$$\begin{aligned}\langle\psi(t)|\Phi_\gamma\rangle &= \left(\frac{1}{\sqrt{3}}e^{i\frac{\omega}{2}t}\langle 0| + \sqrt{\frac{2}{3}}e^{i\pi/4}e^{i\frac{3\omega}{2}t}\langle 1|\right)\left(e^{-\frac{\gamma^2}{2}}\sum_{n=0}^{\infty}\frac{\gamma^n}{\sqrt{n!}}|n\rangle\right)\\ &= e^{-\frac{\gamma^2}{2}}\left(\frac{1}{\sqrt{3}}e^{i\frac{\omega}{2}t} + \gamma\sqrt{\frac{2}{3}}e^{i\pi/4}e^{i\frac{3\omega}{2}t}\right).\end{aligned}$$

Therefore the probability is

$$P_\gamma(t) = e^{-\gamma^2}\left[\frac{1}{3} + \frac{2}{3}\gamma^2 + \frac{2}{3}\gamma(\cos\omega t + \sin\omega t)\right]$$

iii. The probability $P_\gamma(t)$ *can never be 1 since the state* $|\psi(t)\rangle$ *contains only the states* $|0\rangle$ *and* $|1\rangle$, *while the coherent state contains all states* $|n\rangle$ *with amplitudes other than zero.*

More Exercises

19. Consider a particle of mass m in one dimension subject to the potential

$$V(x) = \begin{cases} 0 & 0 < x < L \\ \infty & \text{otherwise} \end{cases}$$

(potential well with infinite walls).
i. Determine the eigenfunctions normalized to 1 and the eigenvalues of the Hamiltonian $\hat{H}$.
ii. Denoting with $|\varphi_n\rangle$ the orthonormal eigenkets of the Hamiltonian $\hat{H}$ and with E_n the respective eigenvalues consider the new Hamiltonian $\hat{H}' = \hat{H} + \lambda|\varphi_i\rangle\langle\varphi_j| + \lambda|\varphi_j\rangle\langle\varphi_i|$ with $i \neq j$. Compute eigenkets and eigenvalues of $\hat{H}'$.

20. Consider a particle of mass m in a potential well with infinitely high walls placed at $x = 0$ and $x = L$. We denote by $\varphi_1(x)$ and $\varphi_2(x)$ the eigenfunctions of the Hamiltonian corresponding to the ground state and the first state excited. The particle comes initially prepared in the state $\psi(x) = C[\varphi_1(x) + \mathrm{i}\varphi_2(x)]$ where C is a positive real constant.
i. Determine C so that $\psi(x)$ is normalized to 1
ii. Determine the wavefunction $\psi(x, t)$ at time t
iii. Indicating with $P(x, t) = |\psi(x, t)|^2$ the probability density at time t and with $J(x, t) = \frac{\hbar}{m}\mathrm{Im}[\psi^*(x, t)\frac{d}{dx}\psi(x, t)]$ the current density at time t verify that the $\psi(x, t)$ calculated in point ii. satisfies the continuity equation $\frac{dP}{dt} + \frac{dJ}{dx} = 0$.
iv. Calculate the probability at time t of finding the particle between 0 and $L/2$.

21. A particle of mass m is constrained to move in a potential well with infinitely high walls in $x = 0$ and $x = L$. The particle has an energy less than $\frac{8\pi^2\hbar^2}{2mL^2}$ and at a certain instant it is in a state for which the probability of finding it in the right half of the well is maximum.
i. Write the normalized wavefunction of that state and calculate the aforementioned probability.
ii. After how long has the probability of the particle being in the right half changed from its maximum to its minimum?

22. A particle of mass m is constrained to move in a potential well with infinitely high walls placed in $x = -L/2$ and $x = L/2$, therefore

$$V(x) = \begin{cases} 0 & |x| < L/2 \\ \infty & \text{otherwise} \end{cases}$$

i. Determine the eigenfunctions normalized to 1 and the eigenvalues of the Hamiltonian $\hat{H}$.
ii. At instant $t = 0$ the particle is described by the wavefunction

$$\Psi(x) = \begin{cases} \sqrt{\frac{2}{L}}\cos\frac{\pi x}{L} & x \in (-\frac{L}{2}, 0) \\ 0 & \text{otherwise} \end{cases}$$

Which energies have non-zero probabilities of being measured?
iii. Determine the wavefunction at time t.

23. A particle of mass m in one dimension is subject to the potential $V(x) = -V_0\theta(L - |x|)$ with $V_0 > 0$ (well with walls of finite hight). Determine the number of bound states as a function of V_0 and L.
24. A particle of mass m in one dimension is subject to the potential

$$V(x) = -a\delta(x + x_0) - a\delta(x - x_0)$$

with $a > 0$. Determine the number of bound states as a function of x_0, their energies and their eigenfunctions.
25. A particle in one dimension is subject to the potential $V(x) = a\delta(x)$ with $a > 0$.
i. Determine the reflection coefficient $\mathcal{R}$ and transmission coefficient $\mathcal{T}$ for all eigenfunctions and verify that $|\mathcal{R}|^2 + |\mathcal{T}|^2 = 1$.
ii. For which energies $|\mathcal{R}| > |\mathcal{T}|$?
26. A particle of mass m in one dimension is subject to the potential

$$V(x) = \begin{cases} \infty & x < 0 \\ \frac{\hbar^2\lambda}{2m}\delta(x - d) & x > 0 \end{cases}$$

with λ and d positive constants
i. Determine eigenfunctions (not necessarily normalized to unity) and eigenvalues of the Hamiltonian
ii. For which eigenvalues of the Hamiltonian do the eigenfunctions not depend on λ?
27. A particle of mass m is constrained to move on a circle of radius R and is not subject to any active force.
i. Using the angle θ as the degree of freedom, write the Hamiltonian of the system.
ii. Using Dirac's postulate calculate the scalar product $\langle\theta|p_\theta\rangle$ between an autobra of the osservable $\hat{\theta}$ and an autoket $|p_\theta\rangle$ of its conjugate moment $\hat{p}_\theta$ with eigenvalue p_θ. Owing any wavefunction $\langle\theta|\Psi\rangle$ be continuous in θ determine the possible eigenvalues of $\hat{p}_\theta$.
iii. Determine the eigenvalues of the Hamiltonian and their degeneracy
28. Let $|n\rangle$ be the eigenket of eigenvalue $\hbar\omega(n + \frac{1}{2})$ of the Hamiltonian of a harmonic oscillator. Indicating as usual with $\hat{x}$ and $\hat{p}$ the position operator and the momentum operator calculate the following average values

$$\langle n|\hat{x}\hat{p}|n\rangle, \qquad \langle n|\hat{p}\hat{x}|n\rangle, \qquad \langle n|\hat{x}\hat{p}\hat{x}|n\rangle, \qquad \langle n|\hat{p}\hat{x}\hat{p}|n\rangle,$$

$$\langle n|\hat{x}\hat{p}|n+1\rangle, \qquad \langle n|\hat{p}\hat{x}|n+1\rangle, \qquad \langle n|\hat{x}\hat{p}\hat{x}|n+1\rangle, \qquad \langle n|\hat{p}\hat{x}\hat{p}|n+1\rangle.$$

29. Consider a particle of mass m subjected to the harmonic potential $V(x) = \frac{1}{2}m\omega^2x^2$. Called $|n\rangle$ the eigenkets of the Hamiltonian and $\hat{a}$ the lowering operator Find the constant C so that it is the ket
$$|\psi\rangle = \frac{C}{1+\lambda\hat{a}}|2\rangle$$
is normalized to 1 for each λ.
ii. Calculate the average value of the $\hat{x}$ operator on the state $|\psi\rangle$.
30. Consider a particle of mass m subjected to the potential $V(x) = bx^2 + cx + d$ with $b > 0$ and c, d arbitrary constants. Calculate eigenfunctions and eigenvalues of Hamiltonian.
31. Let $|\Phi_\gamma\rangle$ be the coherent state of a harmonic oscillator, then $\hat{a}|\Phi_\gamma\rangle = \gamma|\Phi_\gamma\rangle$. Calculate the variances of position and momentum on this state, i.e. $\langle\Phi_\gamma|\hat{\sigma}_x^2|\Phi_\gamma\rangle$ and $\langle\Phi_\gamma|\hat{\sigma}_p^2|\Phi_\gamma\rangle$, and verify that the Heisenberg uncertainty principle is satisfied.
32. Consider a particle of mass m subjected to the potential $V(x) = \frac{1}{2}m\omega^2x^2$ and described by the coherent state $|\Phi_\gamma\rangle$ at time $t = 0$. Indicating with $|\Psi(t)\rangle$ the state of the particle at time t calculate
i. The wave function $\Psi(x, t) = \langle x|\Psi(t)\rangle$ at time t.
ii. The probability density and the probability current al time t.
iii. Verify the continuity equation.
33. Let $|\Phi_\gamma\rangle$ and $|\Phi_{\gamma'}\rangle$ be two coherent states of the same harmonic oscillator. Compute $\langle\Phi_\gamma|\Phi_{\gamma'}\rangle$ for $\gamma = 1/\sqrt{2}$ and $\gamma' = -1/\sqrt{2}$.

Chapter 4
Quantum Particle in Three Dimensions

In this chapter, we address the quantum description of a particle with mass m in three dimensions.

4.1 Momentum Operator and Hamiltonian

In three dimensions, the ket describing the particle at the point $\mathbf{r} = (x, y, z)$ is denoted as $|\mathbf{r}\rangle = |xyz\rangle$, while the ket describing the particle with momentum $\mathbf{p} = (p_x, p_y, p_z)$ is denoted as $|\mathbf{p}\rangle = |p_x p_y p_z\rangle$. Sometimes, for notational simplicity, the position coordinates (x, y, z) are also denoted as (r_1, r_2, r_3), and the momentum coordinates (p_x, p_y, p_z) are also denoted as (p_1, p_2, p_3). Similarly, we denote by $\hat{r}_i$ the i-th component of the position operator and by $\hat{p}_i$ the i-th component of the momentum operator. Therefore

$$\hat{r}_i|\mathbf{r}\rangle = r_i|\mathbf{r}\rangle, \qquad \hat{p}_i|\mathbf{p}\rangle = p_i|\mathbf{p}\rangle. \tag{4.1}$$

As we have already seen in Eqs. (1.130) and (1.134), the scalar product between two position eigenkets and two momentum eigenkets is

$$\langle\mathbf{r}|\mathbf{r}'\rangle = \delta(x - x')\delta(y - y')\delta(z - z') = \delta(r_1 - r_1')\delta(r_2 - r_2')\delta(r_3 - r_3') \tag{4.2}$$

$$\langle\mathbf{p}|\mathbf{p}'\rangle = \delta(p_x - p_x')\delta(p_y - p_y')\delta(p_z - p_z') = \delta(p_1 - p_1')\delta(p_2 - p_2')\delta(p_3 - p_3') \tag{4.3}$$

Meanwhile, according to Eq. (1.141), the scalar product between a position eigenket and a momentum eigenket is the three-dimensional plane wave.

$$\langle\mathbf{r}|\mathbf{p}\rangle = \frac{1}{(2\pi\hbar)^{3/2}}\, e^{\mathrm{i}\frac{\mathbf{p}\cdot\mathbf{r}}{\hbar}} = \frac{1}{(2\pi\hbar)^{3/2}}\, e^{i\frac{p_1 r_1}{\hbar}} e^{i\frac{p_2 r_2}{\hbar}} e^{i\frac{p_3 r_3}{\hbar}}. \tag{4.4}$$

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From this last equation, it is evident that

$$-\mathrm{i}\hbar\frac{\partial}{\partial r_i}\langle\mathbf{r}|\mathbf{p}\rangle = p_i\langle\mathbf{r}|\mathbf{p}\rangle. \tag{4.5}$$

Let us consider a generic ket $|\Psi\rangle$ that describes our particle in three dimensions, and let us learn how to calculate $\langle\mathbf{r}|\hat{p}_i|\Psi\rangle$. By inserting the resolution of the identity in the momentum basis, as seen in Eq. (1.135), and setting $d^3\mathbf{p} \equiv dp_1dp_2dp_3$, we have

$$\begin{aligned}\langle\mathbf{r}|\hat{p}_i|\Psi\rangle &= \int d^3\mathbf{p}\,\langle\mathbf{r}|\hat{p}_i|\mathbf{p}\rangle\langle\mathbf{p}|\Psi\rangle = \int d^3\mathbf{p}\,p_i\langle\mathbf{r}|\mathbf{p}\rangle\langle\mathbf{p}|\Psi\rangle = -\mathrm{i}\hbar\frac{\partial}{\partial r_i}\int d^3\mathbf{p}\,\langle\mathbf{r}|\mathbf{p}\rangle\langle\mathbf{p}|\Psi\rangle \\ &= -\mathrm{i}\hbar\frac{\partial}{\partial r_i}\langle\mathbf{r}|\Psi\rangle,\end{aligned} \tag{4.6}$$

or in vector form

$$\langle\mathbf{r}|\hat{\mathbf{p}}|\Psi\rangle \equiv \begin{pmatrix}\langle\mathbf{r}|\hat{p}_1|\Psi\rangle \\ \langle\mathbf{r}|\hat{p}_2|\Psi\rangle \\ \langle\mathbf{r}|\hat{p}_3|\Psi\rangle\end{pmatrix} = -\mathrm{i}\hbar\begin{pmatrix}\frac{\partial}{\partial r_1}\langle\mathbf{r}|\Psi\rangle \\ \frac{\partial}{\partial r_2}\langle\mathbf{r}|\Psi\rangle \\ \frac{\partial}{\partial r_3}\langle\mathbf{r}|\Psi\rangle\end{pmatrix} = -\mathrm{i}\hbar\boldsymbol{\nabla}\langle\mathbf{r}|\Psi\rangle. \tag{4.7}$$

The scalar product $\Psi(\mathbf{r}) = \langle\mathbf{r}|\Psi\rangle$ is the wave function, already encountered in Sect. 1.4, whose square modulus provides the probability density of finding the electron at $\mathbf{r}$.

The steps just taken can be easily repeated for an arbitrary product $\hat{p}_i\hat{p}_j\hat{p}_k\ldots$. In fact, it is straightforward to verify that

$$(-\mathrm{i}\hbar)\frac{\partial}{\partial r_i}(-\mathrm{i}\hbar)\frac{\partial}{\partial r_j}(-\mathrm{i}\hbar)\frac{\partial}{\partial r_k}\ldots\langle\mathbf{r}|\mathbf{p}\rangle = p_ip_jp_k\ldots\langle\mathbf{r}|\mathbf{p}\rangle \tag{4.8}$$

and hence

$$\langle\mathbf{r}|\hat{p}_i\hat{p}_j\hat{p}_k\ldots|\Psi\rangle = (-\mathrm{i}\hbar)\frac{\partial}{\partial r_i}(-\mathrm{i}\hbar)\frac{\partial}{\partial r_j}(-\mathrm{i}\hbar)\frac{\partial}{\partial r_k}\ldots\Psi(\mathbf{r}). \tag{4.9}$$

In particular we have

$$\langle\mathbf{r}|\hat{p}_i^2|\Psi\rangle = -\hbar^2\frac{\partial^2}{\partial r_i^2}\Psi(\mathbf{r}). \tag{4.10}$$

For conservative forces $\mathbf{F}(\mathbf{r}) = -\nabla V(\mathbf{r})$, the Lagrangian of the system is given by

$$\mathcal{L} = \frac{m}{2}(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) - V(\mathbf{r}) = \frac{m}{2}\sum_i \dot{r}_i^2 - V(\mathbf{r}) \tag{4.11}$$

and therefore the cojugate momenta are

$$p_i = \frac{\partial \mathcal{L}}{\partial \dot{r}_i} = m\dot{r}_i. \tag{4.12}$$

It follows that the Hamiltonian has the following form

$$H = \sum_i p_i \dot{r}_i - \mathcal{L} = \sum_i \frac{p_i^2}{2m} + V(\mathbf{r}) = \frac{p^2}{2m} + V(\mathbf{r}), \tag{4.13}$$

where we have defined $p^2 = \sum_i p_i^2$. The knowledge of the Hamiltonian allows us to write the Schrödinger equation for a particle of mass m in three dimensions

$$\mathrm{i}\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle = \left(\frac{\hat{p}^2}{2m} + V(\hat{\mathbf{r}}) \right) |\Psi(t)\rangle \tag{4.14}$$

where

$$\hat{p}^2 = \sum_i \hat{p}_i^2. \tag{4.15}$$

Note that the potential energy is a function of the position operators $\hat{r}_i$: $V(\hat{\mathbf{r}}) = V(\hat{r}_1, \hat{r}_2, \hat{r}_3) = V(\hat{x}, \hat{y}, \hat{z})$. Therefore, any eigenket $|\mathbf{r}\rangle$ of the three components of the position operator is also an eigenket of $V(\hat{\mathbf{r}})$ with eigenvalue $V(\mathbf{r}) = V(r_1, r_2, r_3) = V(x, y, z)$. We can easily transform the Schrödinger equation into an equation for the wave function $\Psi(\mathbf{r}, t) = \langle \mathbf{r} | \Psi(t) \rangle$ by multiplying on the left by the bra $\langle \mathbf{r}|$. Keeping in mind that $\langle \mathbf{r}| V(\hat{\mathbf{r}}) = \langle \mathbf{r}| V(\mathbf{r})$ and using Eq. (4.10) we find

$$\mathrm{i}\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \left(-\frac{\hbar^2}{2m} \sum_i \frac{\partial^2}{\partial r_i^2} + V(\mathbf{r}) \right) \Psi(\mathbf{r}, t). \tag{4.16}$$

The differential operator

$$\nabla^2 \equiv \sum_i \frac{\partial^2}{\partial r_i^2} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{4.17}$$

is known as the Laplacian, and, in fact, it is the scalar product of two gradients, that is, $\nabla^2 = \boldsymbol{\nabla} \cdot \boldsymbol{\nabla}$, with $\boldsymbol{\nabla} = (\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z})$.

As seen several times before, the knowledge of the eigenfunctions $\varphi_{E,k}(\mathbf{r}) = \langle \mathbf{r} | E, k \rangle$ of the Hamiltonian allows us to determine the temporal evolution. These satisfy

$$\left(\frac{\hat{p}^2}{2m} + V(\hat{\mathbf{r}}) \right) |E, k\rangle = E|E, k\rangle \quad \Rightarrow \quad \left(-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right) \varphi_{E,k}(\mathbf{r}) = E\varphi_{E,k}(\mathbf{r}), \tag{4.18}$$

where, as usual, k is the index used to distinguish eigenfunctions corresponding to the same eigenvalue in case the latter is degenerate. The set of eigenfunctions forms a basis, so we can expand $|\Psi(t)\rangle$ in this basis. In Sect. 1.7, we have shown that the solution is given by

$$|\Psi(t)\rangle = \sum_{E,k} c_{E,k}(0) e^{-\mathrm{i}\frac{Et}{\hbar}} |E,k\rangle \qquad \Rightarrow \qquad \Psi(\mathbf{r},t) = \sum_{E,k} c_{E,k}(0) e^{-\mathrm{i}\frac{Et}{\hbar}} \varphi_{E,k}(\mathbf{r}) \tag{4.19}$$

where

$$c_{E,k}(0) = \langle E,k|\Psi(0)\rangle. \tag{4.20}$$

Note that, similarly to the case of one-dimensional systems, not all functions that satisfy Eq. (4.18) belong to the Hilbert space generated by the physical kets. *The Hilbert space for the eigenfunctions of the Hamiltonian operator is the space of continuous functions such that*

$$\lim_{L\to\infty} \frac{1}{L^3} \int_{-L}^{L} dxdydz\, |\varphi(\mathbf{r})|^2 < \infty. \tag{4.21}$$

So, if for a certain energy E we find a function $\varphi(\mathbf{r})$ that satisfies Eq. (4.18) but $\varphi(\mathbf{r})$ is not continuous or does not satisfy the condition in Eq. (4.21), then this function does not belong to the Hilbert space and, therefore, cannot be considered an eigenfunction.

4.2 Virial Theorem

We want to demonstrate an important result that relates the mean value of the kinetic energy $\hat{T} = \frac{\hat{p}^2}{2m}$ and the mean value of the potential energy $\hat{V} = V(\hat{\mathbf{r}})$ for a generic eigenket of the Hamiltonian $\hat{H} = \hat{T} + \hat{V}$. Consider a generic eigenket $|E,k\rangle$ of $\hat{H}$. It follows

$$\begin{aligned} 0 &= (E-E)\langle E,k|\hat{r}_i\hat{p}_j|E,k\rangle = \langle E,k|\big[\hat{r}_i\hat{p}_j, \hat{H}\big]|E,k\rangle \\ &= \langle E,k|\hat{r}_i\big[\hat{p}_j, V(\hat{\mathbf{r}})\big] + \left[\hat{r}_i, \frac{\hat{p}^2}{2m}\right]\hat{p}_j|E,k\rangle. \end{aligned} \tag{4.22}$$

In the last step, we use the fact that the momentum operator commutes with the kinetic energy, and the position operator commutes with the potential energy. The second commutator is straightforward to calculate and gives

$$\left[\hat{r}_i, \frac{\hat{p}^2}{2m}\right] = \frac{\mathrm{i}\hbar}{m}\hat{p}_i. \tag{4.23}$$

To calculate the first commutator, we can proceed as follows. Let us consider the bracket between two generic kets $|\varphi_1\rangle$ and $|\varphi_2\rangle$:

$$\begin{aligned}\langle\varphi_1|\big[\hat{p}_j, V(\hat{\mathbf{r}})\big]|\varphi_2\rangle &= \int d\mathbf{r}\,\Big(\langle\varphi_1|\mathbf{r}\rangle\langle\mathbf{r}|\hat{p}_j V(\hat{\mathbf{r}})|\varphi_2\rangle - \langle\varphi_1|V(\hat{\mathbf{r}})|\mathbf{r}\rangle\langle\mathbf{r}|\hat{p}_j|\varphi_2\rangle\Big)\\ &= -\mathrm{i}\hbar\int d\mathbf{r}\,\Big(\varphi_1^*(\mathbf{r})\frac{\partial}{\partial r_j}\big(V(\mathbf{r})\varphi_2(\mathbf{r})\big) - \varphi_1^*(\mathbf{r})V(\mathbf{r})\frac{\partial}{\partial r_j}\varphi_2(\mathbf{r})\Big)\\ &= -\mathrm{i}\hbar\int d\mathbf{r}\,\varphi_1^*(\mathbf{r})\frac{\partial V(\mathbf{r})}{\partial r_j}\varphi_2(\mathbf{r}) = -\mathrm{i}\hbar\int d\mathbf{r}\,\langle\varphi_1|\mathbf{r}\rangle\langle\mathbf{r}|\frac{\partial V(\hat{\mathbf{r}})}{\partial r_j}|\varphi_2\rangle\\ &= -\mathrm{i}\hbar\langle\varphi_1|\frac{\partial V(\hat{\mathbf{r}})}{\partial r_j}|\varphi_2\rangle. \end{aligned} \tag{4.24}$$

Since this equation is satisfied for any pair of kets $|\varphi_1\rangle$ e $|\varphi_2\rangle$ we infer that

$$\big[\hat{p}_j, V(\hat{\mathbf{r}})\big] = -\mathrm{i}\hbar\frac{\partial V(\hat{\mathbf{r}})}{\partial r_j}. \tag{4.25}$$

Inserting Eqs. (4.23) and (4.25) in Eq. (4.22) we find

$$\langle E, k|\hat{r}_i\frac{\partial V(\hat{\mathbf{r}})}{\partial r_j}|E, k\rangle = \frac{1}{m}\langle E, k|\hat{p}_i\hat{p}_j|E, k\rangle. \tag{4.26}$$

It's important to emphasize that this identity between average values is satisfied only when the average value is taken over one of the eigenkets of $\hat{H}$. If we replaced $|E, k\rangle$ with a generic ket $|\Psi\rangle$, the identity above would not be satisfied.

Alright, now let us consider the case where $i = j$ and sum over all three components. We obtain $\frac{1}{m}\sum_i \hat{p}_i^2 = 2\hat{T}$ where $\hat{T}$ is the kinetic energy operator. From this, we conclude that

$$\langle E, k|\hat{\mathbf{r}}\cdot\nabla V(\hat{\mathbf{r}})|E, k\rangle = 2\langle E, k|\hat{T}|E, k\rangle. \tag{4.27}$$

This result is known as the **virial theorem**. The proof presented here in three dimensions is clearly entirely general, and therefore, the virial theorem can also be applied in one or two dimensions. In one dimension, the virial theorem is written as.

$$\langle E, k|\hat{x}\frac{\partial}{\partial x}V(\hat{x})|E, k\rangle = 2\langle E, k|\hat{T}|E, k\rangle. \tag{4.28}$$

Let us examine in detail some simple cases. For the one-dimensional harmonic oscillator, we have $V(x) = \frac{1}{2}m\omega^2x^2$, and therefore, $x\frac{dV(x)}{dx} = 2V(x)$. It follows that

$$\langle\hat{V}\rangle = \langle\hat{T}\rangle, \tag{4.29}$$

where the average is taken over a generic eigenket of the harmonic oscillator.

In one dimension, if the particle is subjected to the potential $V(x) = \lambda x^n$, then $x\frac{dV(x)}{dx} = nV(x)$, and thus the virial theorem tells us thar

$$n\langle \hat{V} \rangle = 2\langle \hat{T} \rangle, \tag{4.30}$$

where the average is taken over a generic eigenket of the Hamiltonian $\hat{H} = \hat{T} + \lambda \hat{x}^n$.

Now, let us consider an anisotropic harmonic oscillator in three dimensions with the potential $V(\mathbf{r}) = \frac{1}{2}m(\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2)$. We have

$$\mathbf{r} \cdot \nabla V(\mathbf{r}) = x\frac{\partial V(\mathbf{r})}{\partial x} + y\frac{\partial V(\mathbf{r})}{\partial y} + z\frac{\partial V(\mathbf{r})}{\partial z} = 2V(\mathbf{r}). \tag{4.31}$$

Therefore the relation

$$\langle \hat{V} \rangle = \langle \hat{T} \rangle, \tag{4.32}$$

is valid in three dimensions as well. As before, the average is taken over a generic eigenket of the three-dimensional harmonic oscillator.

Finally, let's consider the case of a Coulomb potential $V(\mathbf{r}) = -Ze^2/r$ where Ze is the charge of the nucleus, e is the charge of the electron, and $r = \sqrt{x^2 + y^2 + z^2}$ is the distance of the electron from the nucleus. We have

$$\frac{\partial V(\mathbf{r})}{\partial r_i} = \frac{Ze^2}{r^3} r_i \qquad \Rightarrow \qquad \mathbf{r} \cdot \nabla V(\mathbf{r}) = -V(\mathbf{r}), \tag{4.33}$$

and therefore the virial theorem reads

$$\langle \hat{V} \rangle = -2\langle \hat{T} \rangle, \tag{4.34}$$

where the average is taken over a generic eigenket of the Hamiltonian $\hat{H} = \hat{T} - Ze^2/\hat{r}$.

4.3 Separable Hamiltonians

Consider the case in which the potential $V(\mathbf{r})$ can be expressed as the sum of three functions, one depending solely on x, one depending solely on y, and one depending solely on z:

$$V(\mathbf{r}) = V_1(x) + V_2(y) + V_3(z). \tag{4.35}$$

Solving the eigenvalue problem in three dimensions, namely Eq. (4.18), reduces to solving three one-dimensional problems. Let us see how it works. Consider the following three one-dimensional eigenvalue problems:

$$\begin{aligned}
&\left(\frac{\hat{p}_x^2}{2m}+V_1(\hat{x})\right)|E_1,k_1\rangle=E_1|E_1,k_1\rangle \quad\Rightarrow\quad \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V_1(x)\right)\varphi^{(1)}_{E_1,k_1}(x)=E_1\varphi^{(1)}_{E_1,k_1}(x)\\
&\left(\frac{\hat{p}_y^2}{2m}+V_2(\hat{y})\right)|E_2,k_2\rangle=E_2|E_2,k_2\rangle \quad\Rightarrow\quad \left(-\frac{\hbar^2}{2m}\frac{d^2}{dy^2}+V_2(y)\right)\varphi^{(2)}_{E_2,k_2}(y)=E_2\varphi^{(2)}_{E_2,k_2}(y)\\
&\left(\frac{\hat{p}_z^2}{2m}+V_3(\hat{z})\right)|E_3,k_3\rangle=E_3|E_3,k_3\rangle \quad\Rightarrow\quad \left(-\frac{\hbar^2}{2m}\frac{d^2}{dz^2}+V_3(z)\right)\varphi^{(3)}_{E_3,k_3}(z)=E_3\varphi^{(3)}_{E_3,k_3}(z)
\end{aligned} \tag{4.36}$$

where

$$\varphi^{(i)}_{E_i,k_i}=\langle x_i|E_i,k_i\rangle,\qquad i=1,2,3 \tag{4.37}$$

denotes the eigenfunction of the ith problem with eigenvalue E_i and degeneracy index k_i. The total Hamiltonian can be written as

$$\hat{H}=\left(\frac{\hat{p}_x^2}{2m}+V_1(\hat{x})\right)+\left(\frac{\hat{p}_y^2}{2m}+V_2(\hat{y})\right)+\left(\frac{\hat{p}_z^2}{2m}+V_3(\hat{z})\right)=\hat{H}_1+\hat{H}_2+\hat{H}_3. \tag{4.38}$$

The operator $\hat{H}_i$ acts only on the ith degree of freedom. Let us then consider the ket

$$\begin{aligned}
|E_1,k_1;\,E_2,k_2;\,E_3,k_3\rangle &= \int d^3\mathbf{r}|\mathbf{r}\rangle\langle\mathbf{r}|E_1,k_1;\,E_2,k_2;\,E_3,k_3\rangle\\
&\equiv \int d^3\mathbf{r}|\mathbf{r}\rangle\langle x|E_1,k_1\rangle\langle y|E_2,k_2\rangle\langle z|E_3,k_3\rangle\\
&= \int d^3\mathbf{r}|\mathbf{r}\rangle\varphi^{(1)}_{E_1,k_1}(x)\varphi^{(2)}_{E_2,k_2}(y)\varphi^{(3)}_{E_3,k_3}(z).
\end{aligned} \tag{4.39}$$

In the first equality, we simply use the completeness relation $\int d^3\mathbf{r}|\mathbf{r}\rangle\langle\mathbf{r}|=1$. The second line "defines" the scalar product between a position eigenket and the ket in the left hand side, thus defining the ket itself. In the third line, we simply use Eq. (4.37). From the definition, it follows that the ket $|E_1,k_1;\,E_2,k_2;\,E_3,k_3\rangle$ describes a particle that, along the x direction, is neither in a position eigenstate nor in an eigenstate of the conjugate momentum, but is in the k_1th eigenstate of $\hat{H}_1$ with eigenvalue E_1. The same considerations apply to the y and z directions. Therefore, we have

$$\begin{aligned}
\langle\mathbf{r}|\hat{H}_i|E_1,k_1;\,E_2,k_2;\,E_3,k_3\rangle &= \left(-\frac{\hbar^2}{2m}\frac{d^2}{dr_i^2}+V_i(r_i)\right)\varphi^{(1)}_{E_1,k_1}(r_1)\varphi^{(2)}_{E_2,k_2}(r_2)\varphi^{(3)}_{E_3,k_3}(r_3)\\
&= E_i\;\varphi^{(1)}_{E_1,k_1}(r_1)\varphi^{(2)}_{E_2,k_2}(r_2)\varphi^{(3)}_{E_3,k_3}(r_3)\\
&= E_i\;\langle\mathbf{r}|E_1,k_1;\,E_2,k_2;\,E_3,k_3\rangle
\end{aligned} \tag{4.40}$$

Since this equation must hold for all $\mathbf{r}$, we obtain

$$\hat{H}_i|E_1,k_1;\,E_2,k_2;\,E_3,k_3\rangle=E_i|E_1,k_1;\,E_2,k_2;\,E_3,k_3\rangle, \tag{4.41}$$

from which it follows that

$$\hat{H}|E_1, k_1; E_2, k_2; E_3, k_3\rangle = (E_1 + E_2 + E_3)|E_1, k_1; E_2, k_2; E_3, k_3\rangle. \tag{4.42}$$

Thus, the ket in Eq. (4.39) is an eigenket of the total Hamiltonian with an eigenvalue of $E_1 + E_2 + E_3$.

We observe that regardless of the choice of values for k_1, k_2, k_3, the energy of the eigenket is always the same. This implies that the energy $E = E_1 + E_2 + E_3$ is at least as degenerate as the product of the degeneracies of E_1, E_2, and E_3. The reason why the degeneracy of E could be even greater is that there might be different values of E_1, E_2, and E_3 with the same sum. For example, let us suppose that the eigenvalues E_1 are all non-degenerate and given by $E_1 = n_1\mathcal{E}$ with n_1 as a non-negative integer. The same holds for $E_2 = n_2\mathcal{E}$ and $E_3 = n_3\mathcal{E}$. Despite the non-degenerate eigenvalues E_1, E_2, and E_3 in their respective one-dimensional problems, the eigenvalue $E = E_1 + E_2 + E_3 = (n_1 + n_2 + n_3)\mathcal{E}$ is, in general, degenerate. For example, the eigenvalue $E = \mathcal{E}$ is three times degenerate because we can obtain it by choosing the triplet of integers $(n_1, n_2, n_3) = (1, 0, 0)$ or $(0, 1, 0)$ or $(0, 0, 1)$.

The discussion made so far is not limited to three-dimensional problems. Consider a system with M degrees of freedom $q_1, \ldots, q_M$, and let $p_1, \ldots, p_M$ denote the corresponding conjugate momenta. The Hamiltonian of the system is said to be **separable** if it can be written as

$$\hat{H} = \sum_{i=1}^{M} H_i(\hat{q}_i, \hat{p}_i). \tag{4.43}$$

In this case, we can obtain its eigenstates by separately solving M eigenvalue problems

$$H_i(\hat{q}_i, \hat{p}_i)|E_i, k_i\rangle = E_i|E_i, k_i\rangle, \qquad i = 1, \ldots, M. \tag{4.44}$$

Using the same reasoning as before, we have

$$\begin{aligned} \hat{H}|E_1, k_1; \ldots; E_M, k_M\rangle &= H_1(\hat{q}_1, \hat{p}_1)|E_1, k_1; \ldots; E_M, k_M\rangle \\ &\quad + \cdots \\ &\quad + H_M(\hat{q}_M, \hat{p}_M)|E_1, k_1; \ldots; E_M, k_M\rangle \\ &= (E_1 + \cdots + E_M)|E_1, k_1; \ldots; E_M, k_M\rangle. \end{aligned} \tag{4.45}$$

To summarize, we have found that if the Hamiltonian is separable, then its eigenfunctions are the *product* of the eigenfunctions of the individual subproblems, and the eigenvalues are the *sum* of the eigenvalues of the individual subproblems.

4.4 Quantum Particle in an Electromagnetic Field

In the case of a particle with mass m and charge Q in three dimensions immersed in an electromagnetic field, the forces are non-conservative, and the Lagrangian is given by Eq. (1.87). We rewrite $\mathcal{L}$ below for convenience

$$\mathcal{L}(\{q\}, \{\dot{q}\}, t) = \frac{m}{2} \sum_i \dot{q}_i^2 - Q\phi + \frac{Q}{c} \sum_i \dot{q}_i A_i. \tag{4.46}$$

If the vector potential $\mathbf{A} = 0$, then we recover the case of the previous section, with $V = Q\phi$ being the potential energy associated with the scalar potential ϕ. The conjugate momenta of the degrees of freedom $(q_1, q_2, q_3) = (x, y, z)$ are

$$p_i = \frac{\partial \mathcal{L}}{\partial \dot{q}_i} = m\dot{q}_i + \frac{Q}{c} A_i \qquad \Rightarrow \qquad \dot{q}_i = \frac{1}{m}\left(p_i - \frac{Q}{c} A_i\right), \tag{4.47}$$

and therefore the Hamiltonian of the particle is

$$\begin{aligned} H &= \sum_i p_i \dot{q}_i - \mathcal{L} \\ &= \frac{1}{m} \sum_i p_i \left(p_i - \frac{Q}{c} A_i\right) - \frac{1}{2m} \sum_i \left(p_i - \frac{Q}{c} A_i\right)^2 + Q\phi - \frac{1}{m} \sum_i \left(p_i - \frac{Q}{c} A_i\right) \frac{Q}{c} A_i \\ &= \frac{1}{2m} \sum_i \left(p_i - \frac{Q}{c} A_i\right)^2 + Q\phi \\ &= \frac{1}{2m} \left(\mathbf{p} - \frac{Q}{c}\mathbf{A}\right) \cdot \left(\mathbf{p} - \frac{Q}{c}\mathbf{A}\right) + Q\phi. \end{aligned} \tag{4.48}$$

Knowing the Hamiltonian we can write the Schrödinger equation

$$\mathrm{i}\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle = \frac{1}{2m} \left[\left(\hat{\mathbf{p}} - \frac{Q}{c}\mathbf{A}(\hat{\mathbf{r}}, t)\right) \cdot \left(\hat{\mathbf{p}} - \frac{Q}{c}\mathbf{A}(\hat{\mathbf{r}}, t)\right) + Q\phi(\hat{\mathbf{r}}, t) \right] |\Psi(t)\rangle. \tag{4.49}$$

Similarly to the case in the previous section, both the scalar and vector potentials are functions of the operators $\hat{r}_i$. Therefore, any eigenket $|\mathbf{r}\rangle$ of the three components of the position operator is also an eigenket of $\phi(\hat{\mathbf{r}}, t)$ with eigenvalue $\phi(\mathbf{r}, t) = \phi(r_1, r_2, r_3, t) = \phi(x, y, z, t)$ and of each component of the vector potential $A_i(\hat{\mathbf{r}}, t)$ with eigenvalue $A_i(\mathbf{r}, t) = A_i(r_1, r_2, r_3, t) = A_i(x, y, z, t)$.

As usual, we can transform the Schrödinger equation into an equation for the wave function $\Psi(\mathbf{r}, t) = \langle \mathbf{r} | \Psi(t) \rangle$ by bracketing on the left by the bra $\langle \mathbf{r} |$. Keeping in mind that $\langle \mathbf{r} | \phi(\hat{\mathbf{r}}) = \langle \mathbf{r} | \phi(\mathbf{r})$ and that $\langle \mathbf{r} | A_i(\hat{\mathbf{r}}) = \langle \mathbf{r} | A_i(\mathbf{r})$, and always keeping in mind Eq. (4.9), we have

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t)=\left[\frac{1}{2m}\left(-\mathrm{i}\hbar\boldsymbol{\nabla}-\frac{Q}{c}\mathbf{A}(\mathbf{r},t)\right)\cdot\left(-\mathrm{i}\hbar\boldsymbol{\nabla}-\frac{Q}{c}\mathbf{A}(\mathbf{r},t)\right)+Q\phi(\mathbf{r},t)\right]\Psi(\mathbf{r},t). \tag{4.50}$$

Let us manipulate the quantity in square brackets. To avoid overly burdening the notation, the dependence on **r** and t will be understood. This yields.

$$\begin{aligned}\left(-\mathrm{i}\hbar\boldsymbol{\nabla}-\frac{Q}{c}\mathbf{A}\right)\cdot\left(-\mathrm{i}\hbar\boldsymbol{\nabla}-\frac{Q}{c}\mathbf{A}\right)\Psi &=\left(-\mathrm{i}\hbar\boldsymbol{\nabla}-\frac{Q}{c}\mathbf{A}\right)\left(-\mathrm{i}\hbar(\boldsymbol{\nabla}\Psi)-\frac{Q}{c}\mathbf{A}\Psi\right)\\ &=\left[-\hbar^2\nabla^2+\frac{\mathrm{i}\hbar Q}{c}(\boldsymbol{\nabla}\cdot\mathbf{A})+\frac{2\mathrm{i}\hbar Q}{c}\mathbf{A}\cdot\boldsymbol{\nabla}+\frac{Q^2}{c^2}A^2\right]\Psi,\end{aligned} \tag{4.51}$$

and therefore Eq. (4.50) becomes

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi=-\frac{\hbar^2}{2m}\nabla^2\Psi+\frac{\mathrm{i}\hbar Q}{mc}\mathbf{A}\cdot\boldsymbol{\nabla}\Psi+\left[Q\phi+\frac{\mathrm{i}\hbar Q}{2mc}(\boldsymbol{\nabla}\cdot\mathbf{A})+\frac{Q^2}{2mc^2}A^2\right]\Psi. \tag{4.52}$$

4.4.1 Continuity Equation

From the Schrödinger equation in Eq. (4.52), we can generalize the continuity equation of one-dimensional systems derived in Sect. 3.1.1. The idea to obtain this generalization is very similar to the one-dimensional case. Multiplying Eq. (4.52) by Ψ^*, we find

$$\mathrm{i}\hbar\Psi^*\frac{\partial\Psi}{\partial t}=-\frac{\hbar^2}{2m}\Psi^*\nabla^2\Psi+\frac{\mathrm{i}\hbar Q}{mc}\Psi^*\mathbf{A}\cdot\boldsymbol{\nabla}\Psi+\left[Q\phi+\frac{\mathrm{i}\hbar Q}{2mc}(\boldsymbol{\nabla}\cdot\mathbf{A})+\frac{Q^2}{2mc^2}A^2\right]|\Psi|^2. \tag{4.53}$$

Taking the complex conjugate of this equation we obtain

$$-\mathrm{i}\hbar\Psi\frac{\partial\Psi^*}{\partial t}=-\frac{\hbar^2}{2m}\Psi\nabla^2\Psi^*-\frac{\mathrm{i}\hbar Q}{mc}\Psi\mathbf{A}\cdot\boldsymbol{\nabla}\Psi^*+\left[Q\phi-\frac{\mathrm{i}\hbar Q}{2mc}(\boldsymbol{\nabla}\cdot\mathbf{A})+\frac{Q^2}{2mc^2}A^2\right]|\Psi|^2. \tag{4.54}$$

Subtracting this equation to Eq. (4.53)

$$\begin{aligned}\mathrm{i}\hbar\frac{\partial|\Psi|^2}{\partial t}&=-\frac{\hbar^2}{2m}\left[\Psi^*\nabla^2\Psi-\Psi\nabla^2\Psi^*\right]+\frac{\mathrm{i}\hbar Q}{mc}\left[\Psi^*\mathbf{A}\cdot\boldsymbol{\nabla}\Psi+\Psi\mathbf{A}\cdot\boldsymbol{\nabla}\Psi^*+(\boldsymbol{\nabla}\cdot\mathbf{A})|\Psi|^2\right]\\ &=-\frac{\hbar^2}{2m}\boldsymbol{\nabla}\cdot[\Psi^*\boldsymbol{\nabla}\Psi-\Psi\boldsymbol{\nabla}\Psi^*]+\frac{\mathrm{i}\hbar Q}{mc}\boldsymbol{\nabla}\cdot(\mathbf{A}|\Psi|^2).\\ &=-\mathrm{i}\hbar\boldsymbol{\nabla}\cdot\left[\frac{\hbar}{2mi}(\Psi^*\boldsymbol{\nabla}\Psi-\Psi\boldsymbol{\nabla}\Psi^*)-\frac{Q}{mc}\mathbf{A}|\Psi|^2\right].\end{aligned} \tag{4.55}$$

The quantity $P(\mathbf{r}, t) = |\Psi(\mathbf{r}, t)|^2$ is the probability density of finding an electron in $\mathbf{r}$ at time t. The **continuity equation**

$$\frac{d}{dt} P(\mathbf{r}, t) + \nabla \cdot \mathbf{J}(\mathbf{r}, t) = 0 \tag{4.56}$$

imposes the identification of the probability current with (reintroducing the dependence on position and time)

$$\mathbf{J}(\mathbf{r}, t) = \frac{\hbar}{2m\mathrm{i}}[\Psi^*(\mathbf{r}, t)\nabla\Psi(\mathbf{r}, t) - \Psi(\mathbf{r}, t)\nabla\Psi^*(\mathbf{r}, t)] - \frac{Q}{mc}\mathbf{A}(\mathbf{r}, t)|\Psi(\mathbf{r}, t)|^2. \tag{4.57}$$

4.4.2 Static Electromagnetic Field

Among all possible electric and magnetic fields, those independent of time certainly play a special role given the experimental feasibility of realizing them. A possible choice for the vector potential $\mathbf{A}(\mathbf{r})$ to generate a spatially uniform magnetic field $\mathbf{B}$ is

$$\mathbf{A}(\mathbf{r}) = -\frac{1}{2}\mathbf{r} \times \mathbf{B} \qquad \Rightarrow \qquad A_i(\mathbf{r}) = -\frac{1}{2}\sum_{mn} \varepsilon_{imn} r_m B_n \tag{4.58}$$

with ε_{imn} being the Levi-Civita tensor. In fact, $\mathbf{B} = \nabla \times \mathbf{A}(\mathbf{r})$, and therefore, see also Appendix B,

$$B_k = \sum_{ji} \varepsilon_{kji} \frac{\partial A_i(\mathbf{r})}{\partial r_j} = -\frac{1}{2}\sum_{jimn} \varepsilon_{kji}\varepsilon_{imn}\frac{\partial r_m}{\partial r_j} B_n = -\frac{1}{2}\sum_{jin} \varepsilon_{kji}\varepsilon_{ijn} B_n = \sum_n \delta_{kn} B_n = B_k. \tag{4.59}$$

Since the vector potential is independent of time, the electric field $\mathbf{E}$ is simply given by $\mathbf{E}(\mathbf{r}) = -\nabla\phi(\mathbf{r})$. Let us discover what the Schrödinger equation becomes in this particular case. Substituting the function $\mathbf{A}(\mathbf{r})$ from Eq. (4.58) into the general Hamiltonian of Eq. (4.49) and performing the products, we find[1]

---

[1] In the derivation of the second line we use, see also Appendix B,

$$\hat{\mathbf{p}} \cdot (\hat{\mathbf{r}} \times \mathbf{B}) = \sum_{ijk} \varepsilon_{ijk} \hat{p}_i \hat{r}_j B_k = -\sum_{ijk} \varepsilon_{kji} \hat{r}_j \hat{p}_i B_k = -(\hat{\mathbf{r}} \times \hat{\mathbf{p}}) \cdot \mathbf{B},$$

$$(\hat{\mathbf{r}} \times \mathbf{B}) \cdot \hat{\mathbf{p}} = \sum_{ijk} \varepsilon_{kij} \hat{r}_i B_j \hat{p}_k = -\sum_{ijk} \varepsilon_{jik} \hat{r}_i \hat{p}_k B_j = -(\hat{\mathbf{r}} \times \hat{\mathbf{p}}) \cdot \mathbf{B}$$

$$(\hat{\mathbf{r}} \times \mathbf{B}) \cdot (\hat{\mathbf{r}} \times \mathbf{B}) = \sum_{imnpq} \varepsilon_{imn}\varepsilon_{ipq} \hat{r}_m B_n \hat{r}_p B_q = \sum_{mnpq} (\delta_{mp}\delta_{nq} - \delta_{mq}\delta_{np}) \hat{r}_m B_n \hat{r}_p B_q = \hat{r}^2 B^2 - (\hat{\mathbf{r}} \cdot \mathbf{B})^2$$

.

$$\begin{aligned}\hat{H} &= \frac{\hat{p}^2}{2m} + \frac{Q}{4mc}\left(\hat{\mathbf{p}}\cdot(\hat{\mathbf{r}}\times\mathbf{B}) + (\hat{\mathbf{r}}\times\mathbf{B})\cdot\hat{\mathbf{p}}\right) + \frac{Q^2}{8mc^2}(\hat{\mathbf{r}}\times\mathbf{B})\cdot(\hat{\mathbf{r}}\times\mathbf{B}) + Q\phi(\hat{\mathbf{r}}) \\ &= \frac{\hat{p}^2}{2m} - \frac{Q}{2mc}(\hat{\mathbf{r}}\times\hat{\mathbf{p}})\cdot\mathbf{B} + \frac{Q^2}{8mc^2}(\hat{r}^2B^2 - (\hat{\mathbf{r}}\cdot\mathbf{B})^2) + Q\phi(\hat{\mathbf{r}}). \end{aligned} \tag{4.60}$$

In this equation, a very important operator in quantum mechanics has appeared, namely the angular momentum operator $\hat{\mathbf{r}}\times\hat{\mathbf{p}}$. In the next sections, we introduce the physical and mathematical framework necessary to deal with this operator.

4.5 Angular Momentum

The **angular momentum operator** is a vector of operators and is defined as in classical mechanics

$$\hat{\mathbf{L}} = \hat{\mathbf{r}}\times\hat{\mathbf{p}} = -\hat{\mathbf{p}}\times\hat{\mathbf{r}}. \tag{4.61}$$

Note that despite the non-commutation of the position operator and the momentum operator, the second identity in Eq. (4.61) holds because the vector product only contains combinations $\hat{r}_i\hat{p}_j$ with $i \neq j$, and we know that, according to the sixth postulate, $[\hat{r}_i, \hat{p}_j] = \mathrm{i}\hbar\delta_{ij}$. We indeed have

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y; \qquad \hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z; \qquad \hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x. \tag{4.62}$$

It is easy to verify that all three components are Hermitian operators, i.e., $\hat{L}_i = \hat{L}_i^\dagger$. Equations (4.62) can be rewritten in a compact form using the Levi-Civita tensor

$$\hat{L}_i = \sum_{jk}\varepsilon_{ijk}\hat{r}_j\hat{p}_k \tag{4.63}$$

where, as for the position and momentum operators, we use double notation $(\hat{L}_x, \hat{L}_y, \hat{L}_z) = (\hat{L}_1, \hat{L}_2, \hat{L}_3)$.

From the commutation rules $[\hat{r}_i, \hat{p}_j] = \mathrm{i}\hbar\delta_{ij}$, it is easy to calculate the commutation rules between the components of angular momentum. These, unlike the commutation rules between the components of the position operator, $[\hat{r}_i, \hat{r}_j] = 0$, and between the components of the momentum operator, $[\hat{p}_i, \hat{p}_j] = 0$, yield a non-zero result. In particular

$$[\hat{L}_x, \hat{L}_y] = \mathrm{i}\hbar\hat{L}_z; \qquad [\hat{L}_z, \hat{L}_x] = \mathrm{i}\hbar\hat{L}_y; \qquad [\hat{L}_y, \hat{L}_z] = \mathrm{i}\hbar\hat{L}_x. \tag{4.64}$$

Let us prove the first one as an example. The proof for the other two is entirely analogous. We have

$$\begin{aligned}[\hat{L}_x, \hat{L}_y] &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z] \\ &= [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] - [\hat{y}\hat{p}_z, \hat{x}\hat{p}_z] - [\hat{z}\hat{p}_y, \hat{z}\hat{p}_x] + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z] \\ &= \hat{y}[\hat{p}_z, \hat{z}]\hat{p}_x + \hat{x}[\hat{z}, \hat{p}_z]\hat{p}_y \\ &= -\mathrm{i}\hbar\hat{y}\hat{p}_x + \mathrm{i}\hbar\hat{x}\hat{p}_y \\ &= \mathrm{i}\hbar\hat{L}_z. \end{aligned} \tag{4.65}$$

Even the commutation rules in Eq. (4.64) can be rewritten in a compact form using the Levi-Civita tensor. In fact

$$[\hat{L}_i, \hat{L}_j] = \mathrm{i}\hbar \sum_k \varepsilon_{ijk}\hat{L}_k. \tag{4.66}$$

Equation (4.66) is telling us that it is not possible to find simultaneous eigenkets of the three operators $(\hat{L}_x, \hat{L}_y, \hat{L}_z)$ since they do not commute. However, starting from them, it is possible to construct an operator that commutes with all three. This is the operator **angular momentum squared**

$$\hat{L}^2 = \hat{\mathbf{L}} \cdot \hat{\mathbf{L}} = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = \sum_i \hat{L}_i^2. \tag{4.67}$$

We have

$$\begin{aligned}[\hat{L}^2, \hat{L}_j] = \sum_i [\hat{L}_i^2, \hat{L}_j] &= \sum_i \left(\hat{L}_i[\hat{L}_i, \hat{L}_j] + [\hat{L}_i, \hat{L}_j]\hat{L}_i\right) \\ &= \mathrm{i}\hbar \sum_{ik} \varepsilon_{ijk}(\hat{L}_i\hat{L}_k + \hat{L}_k\hat{L}_i). \end{aligned} \tag{4.68}$$

Since, under the interchange of i and k, the Levi-Civita tensor is antisymmetric while the quantity in parentheses is symmetric, the result of the sum is zero, see Appendix B. In conclusion

$$[\hat{L}^2, \hat{L}_j] = 0. \tag{4.69}$$

Therefore, it is possible to find simultaneous eigenkets of $\hat{L}^2$ and one of the three components $\hat{L}_j$. We follow the convention adopted by many and choose this component to be $\hat{L}_z$.

4.6 Simultaneous Eigenkets of $\hat{L}^2$ and $\hat{L}_z$

Since $\hat{L}^2$ and $\hat{L}_z$ commute and are Hermitian, they have real eigenvalues and admit a common basis of eigenvectors. We write the eigenvalues of $\hat{L}^2$ as $\hbar^2 l(l+1)$ and those of $\hat{L}_z$ as $\hbar m$. Note that the Planck constant has the dimensions of angular momentum, so the unknown quantities $l(l+1)$ and m are dimensionless. Currently, we cannot say anything about l and m except that they are real numbers. Writing the eigenvalue of $\hat{L}^2$ as $\hbar^2 l(l+1)$ is a convenient choice for the presentation that follows. We could have written it as $\hbar^2\sqrt{g}$, and nothing would have changed, except that we would have found less elegant conditions for g than for l. The possible values of $\hbar^2 l(l+1)$ and $\hbar^2\sqrt{g}$ would still be the same.

We can obtain a first condition on l by noting that the eigenvalues of $\hat{L}^2$ cannot be negative. Suppose, for the sake of contradiction, that $\hat{L}^2$ has an eigenvalue $\hbar^2 w$ with $w < 0$, and let $|w\rangle$ be the corresponding normalized eigenket: $\hat{L}^2|w\rangle = \hbar^2 w|w\rangle$. Multiplying this equation by the bra $\langle w|$ gives

$$\langle w|\hat{L}^2/\hbar^2|w\rangle = \sum_i \langle w|\hat{L}_i^2/\hbar^2|w\rangle = w < 0. \tag{4.70}$$

If we now define the kets $|v_i\rangle = (\hat{L}_i/\hbar)|w\rangle$, since the operators $\hat{L}_i$ are Hermitian, we have $\langle v_i| = \langle w|(\hat{L}_i/\hbar)$. Therefore, the inequality in Eq. (4.70) can be rewritten as

$$\sum_i \langle v_i|v_i\rangle = w < 0 \tag{4.71}$$

which is absurd, as the inner product between a bra and its ket cannot be negative. We conclude that $w \geq 0$. Any number greater than or equal to zero can be uniquely written as $l(l+1)$ by choosing $l \geq 0$. Therefore, from now on, we consider l as a non-negative real number.

Let us also give a name to the simultaneous eigenket of $\hat{L}^2$ and $\hat{L}_z$ with eigenvalues $\hbar^2 l(l+1)$ and $\hbar m$, respectively. Since l and m uniquely identify the eigenvalues, we call $|l, m\rangle$ the corresponding normalized eigenket. Therefore

$$\hat{L}^2|l,m\rangle = \hbar^2 l(l+1)|l,m\rangle, \qquad \hat{L}_z|l,m\rangle = \hbar m|l,m\rangle, \tag{4.72}$$

and

$$\langle l,m|l,m\rangle = 1. \tag{4.73}$$

Now we demonstrate that, for a fixed l, if $\hbar m$ is a possible eigenvalue of $\hat{L}_z$, then $\hbar(m+1)$ and $\hbar(m-1)$ are also eigenvalues of $\hat{L}_z$. To do this, we construct the operators

$$\hat{L}_+ = \hat{L}_x + \mathrm{i}\hat{L}_y, \qquad \hat{L}_- = \hat{L}_x - \mathrm{i}\hat{L}_y = (\hat{L}_+)^\dagger \tag{4.74}$$

Using the commutation rules in Eq. (4.64) we find

$$[\hat{L}_z, \hat{L}_\pm] = [\hat{L}_z, \hat{L}_x \pm \mathrm{i}\hat{L}_y] = \mathrm{i}\hbar\hat{L}_y \pm \mathrm{i}(-\mathrm{i}\hbar)\hat{L}_x = \pm\hbar(\hat{L}_x \pm \mathrm{i}\hat{L}_y) = \pm\hbar\hat{L}_\pm, \tag{4.75}$$

and

$$[\hat{L}_+, L_-] = [\hat{L}_x + \mathrm{i}\hat{L}_y, \hat{L}_x - \mathrm{i}\hat{L}_y] = -\mathrm{i}[\hat{L}_x, \hat{L}_y] + \mathrm{i}[\hat{L}_y, \hat{L}_x] = 2\hbar\hat{L}_z. \quad (4.76)$$

Very well, let us now define the following ket

$$|\Psi_\pm\rangle \equiv \hat{L}_\pm|l, m\rangle. \quad (4.77)$$

Is this ket an eigenket of $\hat{L}^2$? If so, what is its eigenvalue? Let's find out.

$$\begin{aligned}\hat{L}^2|\Psi_\pm\rangle &= \hat{L}^2\hat{L}_\pm|l, m\rangle = \hat{L}^2(\hat{L}_x \pm \mathrm{i}\hat{L}_y)|l, m\rangle = (\hat{L}_x \pm \mathrm{i}\hat{L}_y)\hat{L}^2|l, m\rangle \\ &= \hbar^2 l(l+1)\hat{L}_\pm|l, m\rangle \\ &= \hbar^2 l(l+1)|\Psi_\pm\rangle. \end{aligned} \quad (4.78)$$

So, $|\Psi_\pm\rangle$ is an eigenket of $\hat{L}^2$ with the same eigenvalue as the ket $|l, m\rangle$. What about $\hat{L}_z$? Is $|\Psi_\pm\rangle$ also an eigenket of $\hat{L}_z$? If so, what is its eigenvalue? Let us find out. Taking into account the commutation rule in Eq. (4.75), we have

$$\begin{aligned}\hat{L}_z|\Psi_\pm\rangle &= \hat{L}_z\hat{L}_\pm|l, m\rangle = \left([\hat{L}_z, \hat{L}_\pm] + \hat{L}_\pm\hat{L}_z\right)|l, m\rangle = \left(\pm\hbar\hat{L}_\pm + \hbar m\hat{L}_\pm\right)|l, m\rangle \\ &= \hbar(m \pm 1)|\Psi_\pm\rangle. \end{aligned} \quad (4.79)$$

Therefore $|\Psi_\pm\rangle$ is an eigenket of $\hat{L}_z$ with eigenvalue $\hbar(m \pm 1)$.

Since $|\Psi_\pm\rangle$ is a simultaneous eigenket of $\hat{L}^2$ and $\hat{L}_z$ with eigenvalues $\hbar^2 l(l+1)$ and $\hbar(m \pm 1)$, respectively, we must conclude that this ket is proportional to the ket $|l, m \pm 1\rangle$

$$|\Psi_\pm\rangle = \hat{L}_\pm|l, m\rangle = C_\pm|l, m \pm 1\rangle. \quad (4.80)$$

To determine the normalization constant, we can use the normalization condition in Eq. (4.73), which holds for every l and m. We have

$$|C_\pm|^2 = \langle l, m|(\hat{L}_\pm)^\dagger\hat{L}_\pm|l, m\rangle = \langle l, m|\hat{L}_\mp\hat{L}_\pm|l, m\rangle. \quad (4.81)$$

We now observe that

$$\hat{L}_\mp\hat{L}_\pm = (\hat{L}_x \mp \mathrm{i}\hat{L}_y)(\hat{L}_x \pm \mathrm{i}\hat{L}_y) = \hat{L}_x^2 + \hat{L}_y^2 \pm \mathrm{i}[\hat{L}_x, \hat{L}_y] = \hat{L}^2 - \hat{L}_z^2 \mp \hbar\hat{L}_z \quad (4.82)$$

where, in the last step, we rewrite $\hat{L}_x^2 + \hat{L}_y^2$ as $\hat{L}^2 - \hat{L}_z^2$ and use the first commutation rule in Eq. (4.64). Substituting this result into Eq. (4.81), we find

$$\begin{aligned}|C_\pm|^2 &= \langle l, m|\hat{L}^2 - \hat{L}_z^2 \mp \hbar\hat{L}_z|l, m\rangle = \hbar^2\left[l(l+1) - m^2 \mp m\right] \\ &= \hbar^2\left[l(l+1) - m(m \pm 1)\right]. \end{aligned} \quad (4.83)$$

Using this result in Eq. (4.80) we obtain the following important identity

$$\hat{L}_{\pm}|l, m\rangle = \hbar\sqrt{l(l+1) - m(m \pm 1)}\,|l, m \pm 1\rangle. \tag{4.84}$$

Equation (4.83) imposes constraints on the possible values of m and l. Indeed, if $m > l$, the quantity

$$l(l+1) - m(m+1) < 0, \tag{4.85}$$

which is impossible since $|C_+|^2 > 0$. Similarly, if $m = -|m| < -l$, the quantity

$$l(l+1) - m(m-1) = l(l+1) - |m|(|m|+1) < 0, \tag{4.86}$$

which is impossible since $|C_-|^2 > 0$. Therefore, for a fixed l, m must be between $-l$ and l. For $m = l$, Eq. (4.84) implies that

$$\hat{L}_{+}|l, l\rangle = \hbar\sqrt{l(l+1) - l(l+1)}\,|l, l+1\rangle = |\emptyset\rangle. \tag{4.87}$$

So, the action of $\hat{L}_+$ on $|l, l\rangle$ does not generate another eigenket, which is consistent with the fact that m cannot exceed l. Similarly, for $m = -l$, Eq. (4.84) implies that

$$\hat{L}_{-}|l, -l\rangle = \hbar\sqrt{l(l+1) + l(-l-1)}\,|l, -l-1\rangle = |\emptyset\rangle. \tag{4.88}$$

So, the action of $\hat{L}_-$ on $|l, -l\rangle$ does not generate another eigenket, which is consistent with the fact that m cannot be less than $-l$. Now, if $m = -l$ is a possible eigenvalue, then applying $\hat{L}_+$ to $|l, -l\rangle$ generates a ket proportional to $|l, -l+1\rangle$, see Eq. (4.84). Applying $\hat{L}_+$ to $|l, -l+1\rangle$ generates a ket proportional to $|l, -l+2\rangle$. Continuing to apply $\hat{L}_+$, we must necessarily arrive at the ket $|l, l\rangle$. Indeed, only in this way can the action of $\hat{L}_+$ stop, see Eq. (4.88), and thus only in this way can m not exceed l. This implies that the difference between l and $-l$ must necessarily be an integer k:

$$l - (-l) = 2l = k \quad \Rightarrow \quad l = \frac{k}{2}. \tag{4.89}$$

We conclude that the possible simultaneous eigenkets of $\hat{L}^2$ and $\hat{L}_z$ are the kets $|l, m\rangle$ where l is a half-integer, and $m = -l, -l+1, \ldots, l-1, l$. It is important to note that to reach this conclusion, *we have exclusively used the commutation rules in Eq.* (4.64) *and not the explicit form of the angular momentum operators in Eq.* (4.62). As we see in the next sections, in the case of the angular momentum operators in Eq. (4.62), we are forced to discard some of the possible eigenvalues found. However, the reader should keep in mind that there could be other operators that satisfy the same commutation rules in Eq. (4.64) but are not related to the angular momentum. If these operators exist (and they do exist) we already know the possible form of their eigenvalues and eigenkets.

4.7 Angular Momentum in Polar Coordinates

The angular momentum operator is an observable, and like all observables, it acts on the Hilbert space $\mathcal{H}$ to which the kets describing our particle in three dimensions belong. Given a generic ket $|\Psi\rangle \in \mathcal{H}$, we want to learn how to calculate $\hat{L}_i|\Psi\rangle$. As done previously with the momentum operator, one possible way to perform this calculation is to work in the basis of the position eigenkets. Using Eq. (4.6) and the definition of the angular momentum operator $\hat{L}_i$ in Eq. (4.63), we have

$$\langle \mathbf{r}|\hat{L}_i|\Psi\rangle = \sum_{jk} \varepsilon_{ijk}\langle \mathbf{r}|\hat{r}_j\hat{p}_k|\Psi\rangle = -\mathrm{i}\hbar\sum_{jk}\varepsilon_{ijk}r_j\frac{\partial}{\partial r_k}\langle \mathbf{r}|\Psi\rangle = -\mathrm{i}\hbar\sum_{jk}\varepsilon_{ijk}r_j\frac{\partial}{\partial r_k}\Psi(\mathbf{r}), \tag{4.90}$$

or, in vector form,

$$\langle \mathbf{r}|\hat{\mathbf{L}}|\Psi\rangle \equiv \begin{pmatrix} \langle \mathbf{r}|\hat{L}_x|\Psi\rangle \\ \langle \mathbf{r}|\hat{L}_y|\Psi\rangle \\ \langle \mathbf{r}|\hat{L}_z|\Psi\rangle \end{pmatrix} = -\mathrm{i}\hbar \begin{pmatrix} (y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y})\Psi(\mathbf{r}) \\ \\ (z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z})\Psi(\mathbf{r}) \\ \\ (x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})\Psi(\mathbf{r}) \end{pmatrix} = -\mathrm{i}\hbar\,\mathbf{r}\times\nabla\Psi(\mathbf{r}). \tag{4.91}$$

The calculation of the quantity on the right-hand side is particularly simple if we work in polar coordinates. These coordinates are particularly convenient when the potential energy V depends only on the magnitude of the vector $\mathbf{r}$. In such cases, the Hamiltonian is invariant under rotations, meaning that H is written in the same way whether we use the coordinates x, y, z of our system S or the coordinates x', y', z' of a system S' arbitrarily rotated with respect to S, as $|\mathbf{r}| = |\mathbf{r}'|$ and $\nabla^2 = \nabla' \cdot \nabla'$. These types of potentials are called **central potentials**, and we delve into them later.

In polar coordinates, every point in space is represented by a vector whose coordinates are not the dot product of the vector with the Cartesian unit vector triad $\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z$ but with the polar unit vector triad $\mathbf{e}_r$, $\mathbf{e}_\theta$, and $\mathbf{e}_\phi$. The polar unit vectors are mutually orthogonal, just like $\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z$, but their direction depends on the chosen origin, see Fig. 4.1. The radial unit vector $\mathbf{e}_r$ has the following components in the Cartesian coordinate system x, y, z:

$$\mathbf{e}_r = \begin{pmatrix} \sin\theta\cos\phi \\ \sin\theta\sin\phi \\ \cos\theta \end{pmatrix} = \sin\theta\cos\phi\,\mathbf{e}_x + \sin\theta\sin\phi\,\mathbf{e}_y + \cos\theta\mathbf{e}_z. \tag{4.92}$$

The unit vector $\mathbf{e}_\theta$ can be obtained from the unit vector $\mathbf{e}_r$ by increasing the angle θ by 90°: $\theta \to \theta + \frac{\pi}{2}$. The unit vector $\mathbf{e}_\phi$ can be obtained from the unit vector $\mathbf{e}_r$ by setting $\theta = \frac{\pi}{2}$ (the unit vector $\mathbf{e}_\phi$ is independent of θ) and then increasing the angle ϕ by 90°: $\phi \to \phi + \frac{\pi}{2}$. Taking into account that $\sin\left(\theta + \frac{\pi}{2}\right) = \cos\theta$ and $\cos\left(\theta + \frac{\pi}{2}\right) = -\sin\theta$, we have

$$\mathbf{e}_\theta = \begin{pmatrix} \cos\theta\cos\phi \\ \cos\theta\sin\phi \\ -\sin\theta \end{pmatrix} \qquad \mathbf{e}_\phi = \begin{pmatrix} -\sin\phi \\ \cos\phi \\ 0 \end{pmatrix} \tag{4.93}$$

The convenience of this reference system is that a generic vector $\mathbf{r}$ with magnitude r can simply be expressed as

$$\mathbf{r} = r\,\mathbf{e}_r. \tag{4.94}$$

Now, let us consider the gradient. In Cartesian coordinates, it is

$$\nabla = \mathbf{e}_x\frac{\partial}{\partial x} + \mathbf{e}_y\frac{\partial}{\partial y} + \mathbf{e}_z\frac{\partial}{\partial z}. \tag{4.95}$$

In polar coordinates, we simply need to replace the unit vectors $\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z$ with $\mathbf{e}_r, \mathbf{e}_\theta, \mathbf{e}_\phi$ and then replace the infinitesimal increments ∂x, ∂y, ∂z along the directions $\mathbf{e}_x$, $\mathbf{e}_y$, $\mathbf{e}_z$ with the infinitesimal increments, which we determine shortly, along the directions $\mathbf{e}_r$, $\mathbf{e}_\theta$, $\mathbf{e}_\phi$. Let $\mathbf{r} = r\mathbf{e}_r$ represent a generic point in space. Following a change ∂r in the magnitude r, a change $\partial\theta$ in the angle θ, and a change $\partial\phi$ in the angle ϕ, the new point, see Fig. 4.1, is located at

$$\mathbf{r}' = \mathbf{r} + \mathbf{e}_r\,\partial r + \mathbf{e}_\theta\,r\partial\theta + \mathbf{e}_\phi\,r\sin\theta\partial\phi. \tag{4.96}$$

So, the infinitesimal increment along $\mathbf{e}_r$ is ∂r, the infinitesimal increment along $\mathbf{e}_\theta$ is $r\partial\theta$, and the infinitesimal increment along $\mathbf{e}_\phi$ is $r\sin\theta\partial\phi$. Therefore, the gradient in polar coordinates is written as follows:

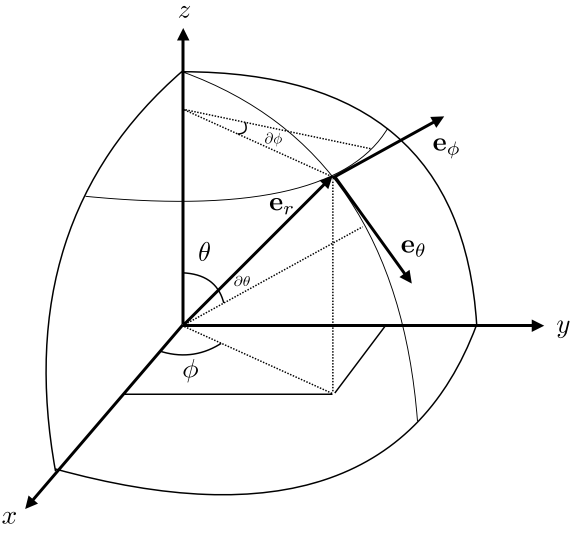

Fig. 4.1 Polar unit vectors $\mathbf{e}r$, $\mathbf{e}\theta$, and $\mathbf{e}_\phi$ and their projections onto the Cartesian axes

$$\boldsymbol{\nabla} = \mathbf{e}_r \frac{\partial}{\partial r} + \frac{\mathbf{e}_\theta}{r}\frac{\partial}{\partial \theta} + \frac{\mathbf{e}_\phi}{r\sin\theta}\frac{\partial}{\partial \phi}. \tag{4.97}$$

We are now ready to express the differential operator $\mathbf{r} \times \boldsymbol{\nabla}$ in polar coordinates. We have:

$$\mathbf{r} \times \boldsymbol{\nabla} = r\,\mathbf{e}_r \times \left(\mathbf{e}_r \frac{\partial}{\partial r} + \frac{\mathbf{e}_\theta}{r}\frac{\partial}{\partial \theta} + \frac{\mathbf{e}_\phi}{r\sin\theta}\frac{\partial}{\partial \phi}\right). \tag{4.98}$$

Using the right-hand rule to evaluate the vector products, we have $\mathbf{e}_r \times \mathbf{e}_r = 0$, $\mathbf{e}_r \times \mathbf{e}_\theta = \mathbf{e}_\phi$ and $\mathbf{e}_r \times \mathbf{e}_\phi = -\mathbf{e}_\theta$. Hence

$$\mathbf{r} \times \boldsymbol{\nabla} = \mathbf{e}_\phi \frac{\partial}{\partial \theta} - \frac{\mathbf{e}_\theta}{\sin\theta}\frac{\partial}{\partial \phi} = \begin{pmatrix} -\sin\phi \\ \cos\phi \\ 0 \end{pmatrix} \frac{\partial}{\partial \theta} - \begin{pmatrix} \cos\theta\cos\phi \\ \cos\theta\sin\phi \\ -\sin\theta \end{pmatrix} \frac{1}{\sin\theta}\frac{\partial}{\partial \phi}. \tag{4.99}$$

From this equation, we can easily extract the x, y, and z components to be inserted into the vector equation Eq. (4.91). We have

$$\langle \mathbf{r}|\hat{L}_x|\Psi\rangle = -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \text{cotg}\theta\cos\phi\frac{\partial}{\partial\phi}\right)\Psi(\mathbf{r}), \tag{4.100}$$

$$\langle \mathbf{r}|\hat{L}_y|\Psi\rangle = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \text{cotg}\theta\sin\phi\frac{\partial}{\partial\phi}\right)\Psi(\mathbf{r}), \tag{4.101}$$

$$\langle \mathbf{r}|\hat{L}_z|\Psi\rangle = -i\hbar\frac{\partial}{\partial\phi}\Psi(\mathbf{r}). \tag{4.102}$$

The other operator whose action we are interested in evaluating is the operator $\hat{L}^2$. In this case as well, its action on a general ket in Hilbert space simplifies when working in polar coordinates. Taking Eq. (4.91) into account, we have:

$$\begin{aligned}
\langle \mathbf{r}|\hat{L}^2|\Psi\rangle &= \langle \mathbf{r}|\hat{\mathbf{L}}\cdot\hat{\mathbf{L}}|\Psi\rangle = -\hbar^2\ (\mathbf{r}\times\boldsymbol{\nabla})\cdot(\mathbf{r}\times\boldsymbol{\nabla})\,\Psi(\mathbf{r}) \\
&= -\hbar^2\left(\mathbf{e}_\phi\frac{\partial}{\partial\theta} - \frac{\mathbf{e}_\theta}{\sin\theta}\frac{\partial}{\partial\phi}\right)\cdot\left(\mathbf{e}_\phi\frac{\partial}{\partial\theta} - \frac{\mathbf{e}_\theta}{\sin\theta}\frac{\partial}{\partial\phi}\right)\Psi(\mathbf{r}) \\
&= -\hbar^2\left(\mathbf{e}_\phi\cdot\frac{\partial\mathbf{e}_\phi}{\partial\theta}\frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\theta^2} - \mathbf{e}_\phi\cdot\frac{\partial\mathbf{e}_\theta}{\partial\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\phi}\right. \\
&\qquad \left. - \frac{\mathbf{e}_\theta}{\sin\theta}\frac{\partial\mathbf{e}_\phi}{\partial\phi}\frac{\partial}{\partial\theta} + \frac{\mathbf{e}_\theta}{\sin^2\theta}\cdot\frac{\partial\mathbf{e}_\theta}{\partial\phi}\frac{\partial}{\partial\phi} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\Psi(\mathbf{r}).
\end{aligned} \tag{4.103}$$

Note that the derivatives of the polar unit vectors are not zero, as they depend on the chosen origin point, as observed earlier. Using Eq. (4.93), we can easily calculate these derivatives. We obtain:

$$\frac{\partial\mathbf{e}_\phi}{\partial\theta} = \frac{\partial}{\partial\theta}\begin{pmatrix} -\sin\phi \\ \cos\phi \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}, \tag{4.104}$$

$$\frac{\partial \mathbf{e}_\phi}{\partial \phi} = \frac{\partial}{\partial \phi}\begin{pmatrix} -\sin\phi \\ \cos\phi \\ 0 \end{pmatrix} = \begin{pmatrix} -\cos\phi \\ -\sin\phi \\ 0 \end{pmatrix}, \tag{4.105}$$

$$\frac{\partial \mathbf{e}_\theta}{\partial \theta} = \frac{\partial}{\partial \theta}\begin{pmatrix} \cos\theta\cos\phi \\ \cos\theta\sin\phi \\ -\sin\theta \end{pmatrix} = \begin{pmatrix} -\sin\theta\cos\phi \\ -\sin\theta\sin\phi \\ -\cos\theta \end{pmatrix}, \tag{4.106}$$

$$\frac{\partial \mathbf{e}_\theta}{\partial \phi} = \frac{\partial}{\partial \phi}\begin{pmatrix} \cos\theta\cos\phi \\ \cos\theta\sin\phi \\ -\sin\theta \end{pmatrix} = \begin{pmatrix} -\cos\theta\sin\phi \\ \cos\theta\cos\phi \\ 0 \end{pmatrix}, \tag{4.107}$$

from which we can evaluate the scalar products that appear in Eq. (4.103):

$$\mathbf{e}_\phi \cdot \frac{\partial \mathbf{e}_\phi}{\partial \theta} = 0 \qquad \mathbf{e}_\phi \cdot \frac{\partial \mathbf{e}_\theta}{\partial \theta} = 0 \qquad \mathbf{e}_\theta \cdot \frac{\partial \mathbf{e}_\phi}{\partial \phi} = -\cos\theta \qquad \mathbf{e}_\theta \cdot \frac{\partial \mathbf{e}_\theta}{\partial \phi} = 0. \tag{4.108}$$

The majority of the scalar products are therefore zero. Substituting these results into Eq. (4.103), we arrive at the final formula

$$\langle \mathbf{r}|\hat{L}^2|\Psi\rangle = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \mathrm{cotg}\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\Psi(\mathbf{r}). \tag{4.109}$$

The results in Eqs. (4.100)–(4.102) and Eq. (4.109) allow us to evaluate the action of the angular momentum operator in the basis of position eigenkets.

4.7.1 Spherical Harmonics

The purpose of this section is to calculate the eigenfunctions of the angular momentum, i.e., the bracket $\langle \mathbf{r}|l, m\rangle$. Multiplying Eqs. (4.72) on the left by the bra $\langle \mathbf{r}|$ and taking into account the previous results, we have

$$\langle \mathbf{r}|\hat{L}^2|l, m\rangle = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \mathrm{cotg}\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\langle \mathbf{r}|l, m\rangle = \hbar^2 l(l+1)\langle \mathbf{r}|l, m\rangle, \tag{4.110}$$

$$\langle \mathbf{r}|\hat{L}_z|l, m\rangle = -i\hbar\frac{\partial}{\partial\phi}\langle \mathbf{r}|l, m\rangle = \hbar m\langle \mathbf{r}|l, m\rangle. \tag{4.111}$$

Similarly, multiplying Eqs. (4.84) on the left by the bra $\langle \mathbf{r}|$ and taking into account the previous results, we have

$$\begin{aligned}\langle \mathbf{r}|\hat{L}_{\pm}|l,m\rangle &= \langle \mathbf{r}|\hat{L}_x \pm \mathrm{i}\hat{L}_y|l,m\rangle \\ &= -\mathrm{i}\hbar\left[(-\sin\phi \pm \mathrm{i}\cos\phi)\frac{\partial}{\partial\theta} - \mathrm{cotg}\theta(\cos\phi \pm \mathrm{i}\sin\phi)\frac{\partial}{\partial\phi}\right]\langle \mathbf{r}|l,m\rangle \\ &= \pm\hbar\, e^{\pm\mathrm{i}\phi}\left[\frac{\partial}{\partial\theta} \pm \mathrm{i}\,\mathrm{cotg}\theta\frac{\partial}{\partial\phi}\right]\langle \mathbf{r}|l,m\rangle = \hbar\sqrt{l(l+1)-m(m\pm 1)}\,\langle \mathbf{r}|l,m\pm 1\rangle.\end{aligned} \tag{4.112}$$

From all these equations, we immediately see that the radial coordinate r is a spectator variable since only the angles θ e ϕ appear in the differential operators. Let us look for a solution of the form:

$$\langle \mathbf{r}|l,m\rangle = R(r)Y_{l,m}(\theta,\phi). \tag{4.113}$$

Substituting this form of $\langle \mathbf{r}|l,m\rangle$ into Eqs. (4.110), (4.111), and (4.112), the radial function $R(r)$ simplifies, and we obtain equations for the functions $Y_{l,m}(\theta,\phi)$ that depend only on the angles:

$$-\left(\frac{\partial^2}{\partial\theta^2} + \mathrm{cotg}\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)Y_{l,m}(\theta,\phi) = l(l+1)Y_{l,m}(\theta,\phi), \tag{4.114}$$

$$-\mathrm{i}\frac{\partial}{\partial\phi}Y_{l,m}(\theta,\phi) = mY_{l,m}(\theta,\phi), \tag{4.115}$$

$$\pm\, e^{\pm\mathrm{i}\phi}\left[\frac{\partial}{\partial\theta} \pm \mathrm{i}\,\mathrm{cotg}\theta\frac{\partial}{\partial\phi}\right]Y_{l,m}(\theta,\phi) = \sqrt{l(l+1)-m(m\pm 1)}\,Y_{l,m\pm 1}(\theta,\phi). \tag{4.116}$$

We observe that if $Y_{l,m}(\theta,\phi)$ satisfies these equations, then the function $\langle \mathbf{r}|l,m\rangle$ in Eq. (4.113) satisfies Eqs. (4.110), (4.111), and (4.112) for any radial function R. This means that there exist infinitely many eigenstates with the same eigenvalues of $\hat{L}^2$ and $\hat{L}_z$ in the Hilbert space $\mathcal{H}$ of our particle in three dimensions. To distinguish them, we can add an additional index R to the ket $|l,m\rangle$, specifying the form of the radial function:

$$|l,m\rangle \to |R,l,m\rangle. \tag{4.117}$$

The bracket

$$\langle \mathbf{r}|R,l,m\rangle = R(r)Y_{l,m}(\theta,\phi) \tag{4.118}$$

yields a radial function characterized by the index R. The most suitable choice of radial functions to form an orthonormal basis on which to expand any wave function $\Psi(\mathbf{r})$ depends on the specific problem at hand, and at the moment, it is not of concern to us. Therefore, let us assume that we have fixed the radial part of all the brackets $\langle \mathbf{r}|l,m\rangle$ and focus on the angular part. In the following we want to find the explicit form of the functions $Y_{l,m}(\theta,\phi)$, also known as **spherical harmonics**.

The solution to Eq. (4.115) is straightforward since the differential operator does not depend on θ, making θ a spectator variable. Therefore, we seek a solution, as already done in Eq. (4.113), that is the product of a function depending on θ and a function depending on ϕ:

$$Y_{l,m}(\theta,\phi) = \Theta_{l,m}(\theta) f_m(\phi). \tag{4.119}$$

Substituting into Eq. (4.115), we see that the function $\Theta_{l,m}(\theta)$ simplifies, and we obtain a differential equation for f_m:

$$-\mathrm{i}\frac{\partial}{\partial\phi} f_m(\phi) = m f_m(\phi), \tag{4.120}$$

the most general solution of which is

$$f_m(\phi) = B_m e^{\mathrm{i}m\phi}, \tag{4.121}$$

where B_m is an arbirary complex constant. Note that for $f_m(\phi)$ to satisfy $f_m(\phi) = f_m(\phi + 2\pi)$, a necessary condition for the continuity of the wave function, the index m cannot be a half-integer. Therefore, among all the possible eigenvalues of $\hat{L}^2$ and $\hat{L}_z$ discussed in Eq. (4.89), we must keep only those for which l is an integer, ensuring that m is automatically an integer. The integer m of the spherical harmonics is called the **azimuthal quantum number**.

Now that we have determined the form of f_m, let us move on to determining the form of $\Theta_{l,m}$. For $m = l$, Eq. (4.116) with the plus sign tells us that:

$$e^{\mathrm{i}\phi}\left[\frac{\partial}{\partial\theta} + \mathrm{i}\mathrm{cotg}\theta\frac{\partial}{\partial\phi}\right] Y_{l,l}(\theta,\phi) = 0. \tag{4.122}$$

Substituting the form of $Y_{l,l}$ from Eq. (4.119), taking the derivative with respect to ϕ, and simplifying, we obtain a differential equation for the function $\Theta_{l,l}(\theta)$.

$$\left[\frac{\partial}{\partial\theta} - l\,\mathrm{cotg}\theta\right]\Theta_{l,l}(\theta) = 0. \tag{4.123}$$

This equation too can be easily solved. Dividing everything by $(\sin\theta)^l$, we get

$$\frac{1}{(\sin\theta)^l}\frac{\partial\Theta_{l,l}(\theta)}{\partial\theta} - l\frac{\cos\theta\,\Theta_{l,l}(\theta)}{(\sin\theta)^{l+1}} = \frac{\partial}{\partial\theta}\left(\frac{\Theta_{l,l}(\theta)}{(\sin\theta)^l}\right) = 0, \tag{4.124}$$

the most general solution of which is

$$\Theta_{l,l}(\theta) = A_l(\sin\theta)^l, \tag{4.125}$$

where A_l is an arbitrary complex constant. In conclusion, the sperical harmonics $Y_{l,l}(\theta,\varphi)$ can be written as

$$Y_{l,l}(\theta,\varphi) = C_l(\sin\theta)^l e^{\mathrm{i}l\phi}, \tag{4.126}$$

where we have defined $C_l = A_l B_l$. The constant C_l is typically fixed by imposing that the integral over solid angle of the square modulus of the spherical harmonic equals 1:

$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta |Y_{l,l}(\theta,\phi)|^2 = 1. \tag{4.127}$$

From now on, we denote the integral over solid angle in the following way

$$\int d\Omega \equiv \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta. \tag{4.128}$$

For instance, for $l = 0$ we find

$$\int d\Omega\, |Y_{0,0}(\theta,\phi)|^2 = |C_0|^2\, 4\pi, \tag{4.129}$$

and hence

$$C_0 = \frac{1}{\sqrt{4\pi}}, \tag{4.130}$$

while for $l = 1$ we find

$$\int d\Omega\, |Y_{1,1}(\theta,\phi)|^2 = |C_1|^2\, 2\pi \int_0^{\pi} d\theta(\sin\theta)^3 = |C_1|^2 \frac{8\pi}{3} \tag{4.131}$$

and hence

$$C_1 = \sqrt{\frac{3}{8\pi}}. \tag{4.132}$$

Once $Y_{l,l}$ is known, we can generate all the other spherical harmonics using Eq. (4.116) with the minus sign. For example, we can generate $Y_{1,0}$ starting from $Y_{1,1}$. Indeed, by setting $m = l = 1$ in Eq. (4.116), we find

$$-\, e^{-\mathrm{i}\phi}\left[\frac{\partial}{\partial\theta} - \mathrm{i}\mathrm{cotg}\theta\frac{\partial}{\partial\phi}\right] Y_{1,1}(\theta,\phi) = \sqrt{2}\, Y_{1,0}(\theta,\phi), \tag{4.133}$$

and using the explicit form just obtained for $Y_{1,1}$

$$Y_{1,0}(\theta,\phi) = -\frac{1}{\sqrt{2}}\sqrt{\frac{3}{8\pi}}e^{-\mathrm{i}\phi}(\cos\theta + \cos\theta)e^{\mathrm{i}\phi} = -\sqrt{\frac{3}{4\pi}}\cos\theta. \tag{4.134}$$

Once $Y_{1,0}$ is known, we can then generate $Y_{1,-1}$ using again Eq. (4.116) with the minus sign and setting $m = 0$:

$$-e^{-\mathrm{i}\phi}\left[\frac{\partial}{\partial\theta} - \mathrm{i}\mathrm{cotg}\theta\frac{\partial}{\partial\phi}\right]Y_{1,0}(\theta,\phi) = \sqrt{2}\,Y_{1,-1}(\theta,\phi), \tag{4.135}$$

from which it follows that

$$Y_{1,-1}(\theta,\phi) = \frac{1}{\sqrt{2}}\sqrt{\frac{3}{4\pi}}e^{-\mathrm{i}\phi}(-\sin\theta) = -\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{-\mathrm{i}\phi}. \tag{4.136}$$

A final important observation. The normalization to unity of the spherical harmonics $Y_{l,l}$ allows us to derive a relationship of orthonormality among all spherical harmonics. Indeed, since the kets $|l,m\rangle$ are all orthonormal, we have

$$\begin{aligned}\delta_{l,l'}\delta_{m,m'} &= \langle l,m|l',m'\rangle = \int d^3\mathbf{r}\langle l,m|\mathbf{r}\rangle\langle\mathbf{r}|l',m'\rangle \\ &= \int_0^\infty dr\, r^2|R(r)|^2 \int d\Omega\; Y^*_{l,m}(\theta,\phi)Y_{l',m'}(\theta,\phi),\end{aligned} \tag{4.137}$$

where in the second equality, we use the resolution of the identity in the coordinate space. For $l = l'$ and $m = m' = l$, the integral over the solid angle is equal to 1, and therefore, the radial integral must also be equal to 1: $\int_0^\infty dr, r^2|R(r)|^2 = 1$. Substituting this result into Eq. (4.137), we find the sought orthonormality relation

$$\int d\Omega\, Y^*_{l,m}(\theta,\phi)Y_{l',m'}(\theta,\phi) = \delta_{l,l'}\delta_{m,m'}. \tag{4.138}$$

4.7.2 Laplacian in Polar Coordinates

As seen in Eq. (4.16), the Schrödinger equation for a particle in three dimensions contains the Laplacian operator. Here, we want to derive the expression of the Laplacian ∇^2 in polar coordinates and demonstrate an important relationship between ∇^2 and the differential operator representing $\hat{L}^2$, see Eq. (4.110). From the expression of the gradient in polar coordinates, see Eq. (4.97), we have:

$$\nabla^2 = \nabla\cdot\nabla = \left[\mathbf{e}_r\frac{\partial}{\partial r} + \frac{1}{r}\left(\mathbf{e}_\theta\frac{\partial}{\partial\theta} + \frac{\mathbf{e}_\phi}{\sin\theta}\frac{\partial}{\partial\phi}\right)\right]\cdot\left[\mathbf{e}_r\frac{\partial}{\partial r} + \frac{1}{r}\left(\mathbf{e}_\theta\frac{\partial}{\partial\theta} + \frac{\mathbf{e}_\phi}{\sin\theta}\frac{\partial}{\partial\phi}\right)\right]. \tag{4.139}$$

The calculation we need to perform is very similar to the calculation we have already carried out to evaluate the action of $\hat{L}^2$ in Eq. (4.103). Since the polar unit vectors do not depend on r, their derivative with respect to r is zero. Therefore, using the orthogonality between the unit vectors, we obtain a first simplification:

$$\begin{aligned}\nabla^2 &= \frac{\partial^2}{\partial r^2} + \left[\frac{1}{r}\left(\mathbf{e}_\theta \frac{\partial}{\partial \theta} + \frac{\mathbf{e}_\phi}{\sin\theta}\frac{\partial}{\partial \phi}\right)\right] \cdot \left[\mathbf{e}_r \frac{\partial}{\partial r} + \frac{1}{r}\left(\mathbf{e}_\theta \frac{\partial}{\partial \theta} + \frac{\mathbf{e}_\phi}{\sin\theta}\frac{\partial}{\partial \phi}\right)\right] \\ &= \frac{\partial^2}{\partial r^2} + \frac{1}{r}\left(\mathbf{e}_\theta \cdot \frac{\partial \mathbf{e}_r}{\partial \theta} + \frac{\mathbf{e}_\phi}{\sin\theta} \cdot \frac{\partial \mathbf{e}_r}{\partial \phi}\right)\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\mathbf{e}_\theta \frac{\partial}{\partial \theta} + \frac{\mathbf{e}_\phi}{\sin\theta}\frac{\partial}{\partial \phi}\right) \cdot \left(\mathbf{e}_\theta \frac{\partial}{\partial \theta} + \frac{\mathbf{e}_\phi}{\sin\theta}\frac{\partial}{\partial \phi}\right). \end{aligned} \tag{4.140}$$

Now let us calculate the derivatives of the radial unit vector with respect to the angles. From Eq. (4.92), we have:

$$\frac{\partial \mathbf{e}_r}{\partial \theta} = \frac{\partial}{\partial \theta}\begin{pmatrix} \sin\theta\cos\phi \\ \sin\theta\sin\phi \\ \cos\theta \end{pmatrix} = \begin{pmatrix} \cos\theta\cos\phi \\ \cos\theta\sin\phi \\ -\sin\theta \end{pmatrix}, \tag{4.141}$$

$$\frac{\partial \mathbf{e}_r}{\partial \phi} = \frac{\partial}{\partial \phi}\begin{pmatrix} \sin\theta\cos\phi \\ \sin\theta\sin\phi \\ \cos\theta \end{pmatrix} = \begin{pmatrix} -\sin\theta\sin\phi \\ \sin\theta\cos\phi \\ 0 \end{pmatrix}, \tag{4.142}$$

from which we can deduce the value of the following scalar products, see Eq. (4.93),

$$\mathbf{e}_\theta \cdot \frac{\partial \mathbf{e}_r}{\partial \theta} = 1, \qquad \mathbf{e}_\phi \cdot \frac{\partial \mathbf{e}_r}{\partial \phi} = \sin\theta. \tag{4.143}$$

Again, exploiting the orthogonality of the unit vectors, Eq. (4.140) becomes:

$$\begin{aligned}\nabla^2 &= \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\mathbf{e}_\theta \frac{\partial}{\partial \theta} + \frac{\mathbf{e}_\phi}{\sin\theta}\frac{\partial}{\partial \phi}\right) \cdot \left(\mathbf{e}_\theta \frac{\partial}{\partial \theta} + \frac{\mathbf{e}_\phi}{\sin\theta}\frac{\partial}{\partial \phi}\right) \\ &= \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\mathbf{e}_\theta \cdot \frac{\partial \mathbf{e}_\theta}{\partial \theta}\frac{\partial}{\partial \theta} + \frac{\partial^2}{\partial \theta^2} + \mathbf{e}_\theta \cdot \frac{\partial \mathbf{e}_\phi}{\partial \theta}\frac{1}{\sin\theta}\frac{\partial}{\partial \phi}\right. \\ &\quad \left. + \frac{\mathbf{e}_\phi}{\sin\theta} \cdot \frac{\partial \mathbf{e}_\theta}{\partial \phi}\frac{\partial}{\partial \theta} + \frac{\mathbf{e}_\phi}{\sin^2\theta} \cdot \frac{\partial \mathbf{e}_\phi}{\partial \phi}\frac{\partial}{\partial \phi} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right) \end{aligned} \tag{4.144}$$

Now, using Eqs. (4.104), (4.105), (4.106), and (4.107) for the angular unit vectors, we can easily calculate all other scalar products

$$\mathbf{e}_\theta \cdot \frac{\partial \mathbf{e}_\theta}{\partial \theta} = 0, \qquad \mathbf{e}_\theta \cdot \frac{\partial \mathbf{e}_\phi}{\partial \theta} = 0, \qquad \mathbf{e}_\phi \cdot \frac{\partial \mathbf{e}_\theta}{\partial \phi} = \cos\theta, \qquad \mathbf{e}_\phi \cdot \frac{\partial \mathbf{e}_\phi}{\partial \phi} = 0, \tag{4.145}$$

and eventually obtain

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{\partial^2}{\partial \theta^2} + \mathrm{cotg}\theta\frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right). \tag{4.146}$$

The differential operator in parentheses coincides precisely with the operator representing $\hat{L}^2$, compare with Eq. (4.110), apart from a factor of $-\hbar^2$. We can then define the angular part of the Laplacian as

$$\nabla^2_\Omega \equiv \left(\frac{\partial^2}{\partial\theta^2} + \text{cotg}\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right), \tag{4.147}$$

and rewrite Eq. (4.114) according to

$$-\hbar^2 \nabla^2_\Omega Y_{l,m}(\theta,\phi) = \hbar^2 l(l+1) Y_{l,m}(\theta,\phi). \tag{4.148}$$

Finally we observe that

$$\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} = \frac{1}{r}\frac{\partial^2}{\partial r^2} r, \tag{4.149}$$

and thus, we can rewrite the Laplacian in polar coordinates in a more compact form:

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2} r + \frac{1}{r^2}\nabla^2_\Omega. \tag{4.150}$$

4.8 Central Potential

We consider the Schrödinger equation (4.18), in the case of a central potential $V(\mathbf{r}) = V(r)$. Taking into account the result in Eq. (4.150), we have

$$-\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2(r\varphi(\mathbf{r}))}{\partial r^2} - \frac{\hbar^2}{2mr^2}\nabla^2_\Omega \varphi(\mathbf{r}) + V(r)\varphi(\mathbf{r}) = E\varphi(\mathbf{r}). \tag{4.151}$$

This is differential equation for an unknown function that depends on $\mathbf{r}$. We can simplify the problem by working in polar coordinates. Let us look for a solution of the form

$$\varphi(\mathbf{r}) = \langle \mathbf{r} | R, l, m \rangle = R(r) Y_{l,m}(\theta,\phi). \tag{4.152}$$

Taking into account Eq. (4.148), the equation reduces to a differential equation for the sole function $R(r)$:

$$-\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2(rR(r))}{\partial r^2} + \left(\frac{\hbar^2 l(l+1)}{2mr^2} + V(r) \right) R(r) = ER(r). \tag{4.153}$$

It is interesting to note that we have generated an effective potential

$$V_{\text{eff}}(r) = \frac{\hbar^2 l(l+1)}{2mr^2} + V(r) \tag{4.154}$$

given by the sum of the central potential $V(r)$ and the centrifugal potential. This result is not surprising at all. In fact, the wavefunction in Eq. (4.152) is an eigenfunction of the angular momentum and therefore describes a particle with a well-defined angular momentum. Classically, a particle with angular momentum $\hbar l$ at a distance r from the origin has a velocity $v = \frac{\hbar l}{mr}$ and thus a kinetic energy $T = \frac{m}{2}v^2 = \frac{\hbar^2 l^2}{2mr^2}$. Also classically, the centrifugal potential arises from the kinetic energy. The only difference compared to the classical case is that $l^2 \to l(l+1)$. However, this difference is negligible for very large values of l, such as those of macroscopic objects.

The solutions of Eq. (4.153) provide the eigenfunctions of the initial problem once the radial function is multiplied by the spherical harmonic $Y_{l,m}$. Let us then work on this equation. Multiplying it by r and defining

$$\chi(r) = rR(r) \tag{4.155}$$

we obtain

$$-\frac{\hbar^2}{2m}\frac{\partial^2\chi(r)}{\partial r^2} + \left(\frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right)\chi(r) = E\chi(r). \tag{4.156}$$

This equation needs to be solved for all integer values of l, and for each l we find a series of eigenvalues $E_{n,l}$ and corresponding eigenfunctions $\chi_{n,l}$. Both the eigenvalues and eigenfunctions depend, of course, on the nature of the central potential $V(r)$. In the next section, we consider the case of the Coulomb potential

4.9 Hydrogen Atom

Let us consider an electron with charge $-e$ immersed in the potential generated by a positive charge Ze located at the origin of the coordinates. The potential energy is then the Coulombic one and is given by

$$V(r) = -\frac{Ze^2}{r}. \tag{4.157}$$

Finding the eigenfunctions of Eq. (4.156) with the central potential in Eq. (4.157) means finding the eigenfunctions of an electron in a Hydrogen atom when $Z = 1$, in a helium ion when $Z = 2$, in a lithium dication when $Z = 3$, etc. We are therefore about to solve a problem of utmost importance since atoms are the building blocks of matter, and the Hydrogen atom is the simplest among them.

In the case of the Coulomb potential energy, the effective potential in Eq. (4.154) is given by

$$V_{\text{eff}}(r) = \frac{\hbar^2 l(l+1)}{2m_e r^2} - \frac{Ze^2}{r}, \tag{4.158}$$

where we denote the electron's mass as m_e. This potential starts from $+\infty$ at $r = 0$, decreases as r increases until it reaches a minimum value $V_{\min} = -\frac{Z^2 e^4 m_e}{2\hbar^2 l(l+1)} < 0$ at $r = \frac{\hbar^2 Z e^2 l(l+1)}{m_e}$, then begins to increase again while remaining negative, and tends to zero as $r \to \infty$. Classically, the electron remains bound if its energy is less than zero. Quantum mechanically, if the energy is less than zero, we can have bound states, as discussed in Sect. 3.2. We are particularly interested in this occurrence because if the theory did not predict bound states, then we would not be able to explain the stability of the simplest atom that exists in nature, and all the effort made so far would be in vain. We therefore study whether there are solutions with energy $E = -|E| < 0$.

We divide Eq. (4.156) by $|E|$:

$$-\frac{\hbar^2}{2m_e|E|}\frac{\partial^2 \chi(r)}{\partial r^2} + \left(\frac{\hbar^2 l(l+1)}{2m_e|E|r^2} - \frac{Ze^2}{|E|r}\right)\chi(r) = -\chi(r). \tag{4.159}$$

To avoid carrying too many constants with us, we define

$$\kappa^2 \equiv \frac{2m_e|E|}{\hbar^2} > 0 \tag{4.160}$$

and the dimensionless coordinate

$$\rho \equiv \kappa r. \tag{4.161}$$

Then Eq. (4.159) becomes

$$\frac{\partial^2 \chi}{\partial \rho^2} + \left(-1 - \frac{l(l+1)}{\rho^2} + \frac{Ze^2\kappa}{|E|\rho}\right)\chi = 0. \tag{4.162}$$

For convenience we also define the constant

$$\alpha \equiv \frac{Ze^2\kappa}{|E|} = \frac{2m_e Z e^2}{\hbar^2\kappa}, \tag{4.163}$$

and rewrite Eq. (4.162) in terms of α

$$\frac{\partial^2 \chi}{\partial \rho^2} + \left(-1 - \frac{l(l+1)}{\rho^2} + \frac{\alpha}{\rho}\right)\chi = 0. \tag{4.164}$$

We have thus reduced the problem to finding the values of α (and therefore of the energy) for which Eq. (4.164) admits a solution χ different from zero. Let us begin by getting acquainted with this differential equation, studying how the solution behaves in the two limiting cases $\rho \to 0$ and $\rho \to \infty$. For $\rho \to 0$, the dominant contribution in parentheses is that of the centrifugal potential, and we can approximate the equation as

$$\frac{\partial^2 \chi}{\partial \rho^2} - \frac{l(l+1)}{\rho^2}\chi = 0. \tag{4.165}$$

This is a Euler's differential equation since if $\rho \to \lambda\rho$, the equation remains unchanged. The solutions to the Euler's equation are functions of the form $\chi = \rho^q$. It is straightforward to verify that if

$$q(q-1) - l(l+1) = 0, \tag{4.166}$$

and thus if $q = l + 1$ or $q = -l$, then $\chi = \rho^q$ is a solution. Therefore, the most general solution as $\rho \to 0$ is

$$\chi = a_1 \rho^{l+1} + a_2 \rho^{-l}, \tag{4.167}$$

with a_1 and a_2 arbitrary constants. Remembering that the radial function is $R(r) = \chi/r$, see Eq. (4.155), if a_2 were nonzero, then for small r we would have $R(r) = a_2 \kappa^{-l} r^{-l-1}$, which diverges at the origin for every $l \geq 0$. Divergent functions are not continuous; therefore, they do not belong to the Hilbert space and must be discarded. We conclude that for small ρ

$$\chi = a_1 \rho^{l+1}. \tag{4.168}$$

Now let us consider the other limiting case $\rho \to \infty$. In this case, the last two terms in the parentheses of Eq. (4.164) tend to zero, and the equation can be approximated as

$$\frac{\partial^2 \chi}{\partial \rho^2} - \chi = 0. \tag{4.169}$$

whose most general solution is

$$\chi = b_1 e^{\rho} + b_2 e^{-\rho}. \tag{4.170}$$

Again, it is necessary to restrict the generality of this solution because if b_1 were nonzero, the wave function would diverge exponentially, and the condition in Eq. (4.21) could not be satisfied. We conclude that for large ρ

$$\chi = b_2 e^{-\rho}. \tag{4.171}$$

In light of the asymptotic behaviors just discussed, we look for solutions valid for all ρ having the form

$$\chi = e^{-\rho} \rho^{l+1} \sum_{q=0}^{\infty} c_q \rho^q = e^{-\rho} \sum_{q=0}^{\infty} c_q \rho^{q+l+1} = \sum_{q=0}^{\infty} c_q e^{-\rho} \rho^{q+l+1}, \tag{4.172}$$

where the coefficients c_q must be chosen in such a way that χ satisfies Eq. (4.164). We then substitute the expression from Eq. (4.172) into Eq. (4.164). The calculation of the second derivative of χ is easily done

$$\begin{aligned}\frac{\partial^2 \chi}{\partial \rho^2} &= \sum_{q=0}^{\infty} c_q \frac{\partial^2}{\partial \rho^2} e^{-\rho} \rho^{q+l+1} \\ &= \sum_{q=0}^{\infty} c_q \left(e^{-\rho} \rho^{q+l+1} - 2(q+l+1) e^{-\rho} \rho^{q+l} + (q+l+1)(q+l) e^{-\rho} \rho^{q+l-1} \right) \\ &= e^{-\rho} \sum_{q=0}^{\infty} c_q \rho^{q+l+1} \left(1 - 2(q+l+1)\rho^{-1} + (q+l+1)(q+l)\rho^{-2} \right). \end{aligned} \tag{4.173}$$

As for the second term, we find

$$\left(-1 - \frac{l(l+1)}{\rho^2} + \frac{\alpha}{\rho} \right) \chi = e^{-\rho} \sum_{q=0}^{\infty} c_q \rho^{q+l+1} \left(-1 - l(l+1)\rho^{-2} + \alpha \rho^{-1} \right) \tag{4.174}$$

Equation (4.164) tells us that the sum of these last two equations must be zero, which implies that

$$\begin{aligned} & e^{-\rho} \sum_{q=0}^{\infty} c_q \rho^{q+l+1} \left(1 - 2(q+l+1)\rho^{-1} + (q+l+1)(q+l)\rho^{-2} - 1 - l(l+1)\rho^{-2} + \alpha\rho^{-1} \right) \\ &= e^{-\rho} \sum_{q=0}^{\infty} c_q \rho^{q+l} \left[\alpha - 2(q+l+1) \right] \\ &+ e^{-\rho} \sum_{q=0}^{\infty} c_q \rho^{q+l-1} \left[(q+l+1)(q+l) - l(l+1) \right] = 0 \end{aligned} \tag{4.175}$$

In the second sum on the right hand side, the term with $q = 0$ is zero. We can then start the sum from $q = 1$. Writing the index q of the second sum as $q = q' + 1$ so that the sum over q' starts from zero, we find

$$\begin{aligned} & \sum_{q=1}^{\infty} c_q \rho^{q+l-1} \left[(q+l+1)(q+l) - l(l+1) \right] \\ &= \sum_{q'=0}^{\infty} c_{q'+1} \rho^{q'+l} \left[(q'+l+2)(q'+l+1) - l(l+1) \right]. \end{aligned} \tag{4.176}$$

At this point, renaming the dummy index q' to q, we see that Eq. (4.175) can be rewritten as

$$e^{-\rho} \sum_{q=0}^{\infty} \rho^{q+l} \left\{ c_q [\alpha - 2(q+l+1)] + c_{q+1} [(q+l+2)(q+l+1) - l(l+1)] \right\} = 0. \tag{4.177}$$

For this equation to be satisfied, the coefficients of all powers of ρ must be zero. Therefore

$$\begin{aligned} c_q[2(q+l+1)-\alpha] &= c_{q+1}[(q+l+2)(q+l+1)-l(l+1)] \\ &= c_{q+1}[(l+q+1)(l+1+q+1)-l(l+1)] \\ &= c_{q+1}[(q+1)(q+2l+2)]. \end{aligned} \tag{4.178}$$

We find in this way a recursive relation

$$c_{q+1} = \frac{2(q+l+1)-\alpha}{(q+1)(q+2l+2)} c_q \tag{4.179}$$

which allows for determining all coefficients in terms of c_0. Indeed

$$\begin{aligned} c_1 &= \frac{2(0+l+1)-\alpha}{(0+1)(0+2l+2)} c_0 = \frac{2(l+1)-\alpha}{2(l+1)} c_0 \\ c_2 &= \frac{2(1+l+1)-\alpha}{(1+1)(1+2l+2)} c_1 = \frac{2(l+2)-\alpha}{2(2l+3)} \times \frac{2(l+1)-\alpha}{2(l+1)} c_0 \\ \ldots \end{aligned} \tag{4.180}$$

and so on and so forth. Note that except for c_0, which we can fix later with an appropriate normalization, the other coefficients depend on α, which in turn depends on the energy E, see Eq. (4.163). So, for each energy E, Eq. (4.179) generates coefficients $c_q(E)$, which, when inserted into Eq. (4.172), give rise to a function χ_E and therefore to the radial eigenfunction $R_E = \chi_E/r$. It remains to be seen whether we can accept all these solutions or if some of them should be discarded because they do not belong to the Hilbert space. One of the conditions for belonging to the Hilbert space is that Eq. (4.21) holds. Let us study the behavior of the function χ in the limit of large ρ. Let $Q \gg 1$ and separate the expansion in Eq. (4.172) into a sum from $q = 0$ to $q = Q$ and another sum from $q = Q + 1$ to $q = \infty$

$$\chi = \underbrace{e^{-\rho}\rho^{l+1} \sum_{q=0}^{Q} c_q \rho^q}_{P(\rho)} + e^{-\rho}\rho^{l+1} \sum_{q=Q+1}^{\infty} c_q \rho^q \tag{4.181}$$

where $P(\rho)$ is a polynomial of degree $l + Q + 1$. In the limit of large ρ, the term with $P(\rho)$ is suppressed by the exponential, and therefore

$$\lim_{\rho\to\infty} \chi = \lim_{\rho\to\infty} e^{-\rho}\rho^{l+1} \sum_{q=Q+1}^{\infty} c_q \rho^q. \tag{4.182}$$

For very large q, the recursive system of Eq. (4.179) can be approximated as $c_{q+1} = \frac{2}{q} c_q$. We then have

$$\begin{aligned}
\lim_{\rho\to\infty} \chi &= c_Q \lim_{\rho\to\infty} e^{-\rho}\rho^{l+1}\left(\frac{2\rho^{Q+1}}{Q} + \frac{2^2\rho^{Q+2}}{(Q+1)Q} + \frac{2^3\rho^{Q+3}}{(Q+2)(Q+1)Q} + \cdots\right)\\
&= \frac{c_Q}{2^{Q-1}} \lim_{\rho\to\infty} e^{-\rho}\rho^{l+2}\left(\frac{(2\rho)^Q}{Q} + \frac{(2\rho)^{Q+1}}{(Q+1)Q} + \frac{(2\rho)^{Q+2}}{(Q+2)(Q+1)Q} + \cdots\right)\\
&= \frac{c_Q(Q-1)!}{2^{Q-1}} \lim_{\rho\to\infty} e^{-\rho}\rho^{l+2}\sum_{q=Q}^{\infty}\frac{(2\rho)^q}{q!}\\
&= \frac{c_Q(Q-1)!}{2^{Q-1}} \lim_{\rho\to\infty} e^{-\rho}\rho^{l+2}\left(e^{2\rho} - \sum_{q=0}^{Q-1}\frac{(2\rho)^q}{q!}\right) = \frac{c_Q(Q-1)!}{2^{Q-1}} \lim_{\rho\to\infty} e^{\rho}\rho^{l+2}.
\end{aligned} \tag{4.183}$$

So, χ diverges exponentially. This means that the radial function $R = \chi/r$ does not belong to the Hilbert space! The only way for χ to belong to the Hilbert space is that for some q the coefficient c_q is zero. In that case, all coefficients c_m with $m > q$ would also be zero, and the sum in Eq. (4.172) would terminate at the power ρ^{q+l}. But what conditions must be satisfied for this to happen? From Eq. (4.179), this can only occur if α is an even integer. Let us analyze this fact in detail. Suppose that

$$\alpha = 2n. \tag{4.184}$$

In this case, the recursive system for the coefficients c_q becomes

$$c_{q+1} = \frac{2(q+l+1-n)}{(q+1)(q+2l+2)} c_q. \tag{4.185}$$

If the angula moment satisfies

$$l + 1 \leq n, \tag{4.186}$$

we could generate a function χ whose last coefficient is the one with $q = n - l - 1$. Conversely, if α were not an even integer or if $l + 1$ were greater than n, the recursive system would not terminate, and the function χ would diverge exponentially. The integer n is called the **principal quantum number**.

In summary, the only radial eigenfunctions that belong to the Hilbert space have the form

$$R_{n,l}(r) = \frac{\chi_{n,l}(r)}{r} \tag{4.187}$$

where

- the principal quantum number n can take all positive integer values: $n = 1, 2, \dots, \infty$
- At a fixed n, the quantum number l of the angular momentum can take values $l = 0, 1, \dots, n-1$
- $\chi_{n,l}$ is the function in Eq. (4.172) whose coefficients satisfy the recursive system of Eq. (4.179) with $\alpha = 2n$ (and therefore all coefficients c_q with $q > n - l - 1$ are zero).

The condition on α is, in fact, a condition on the possible energies of the Hamiltonian. Indeed, imposing that $\alpha = 2n$ implies, from Eq. (4.163), that only for energies $E = E_n$ where

$$2n = \frac{2m_e Ze^2}{\hbar^2 \kappa} = \frac{\sqrt{2m_e} Ze^2}{\hbar\sqrt{|E_n|}} \qquad \Rightarrow \qquad E_n = -\frac{m_e Z^2 e^4}{2n^2\hbar^2} \tag{4.188}$$

the Schrödinger equation admits physical solutions $\chi_{n,l}$. The E_n are precisely the energies of the bound states and are also called the **energies of the atomic levels**. The energy of the ground state is obtained by setting $n = 1$ and is given by

$$E_1 = -\frac{m_e Z^2 e^4}{2\hbar^2} = -Z^2 \times 13.6\ \text{eV}. \tag{4.189}$$

The energies of the bound states $E_n = E_1/n^2$ are all correctly negative and tend to accumulate as n increases. Furthermore, as in the case of one-dimensional problems, they are quantized. In Fig. 4.2, we show the position of the quantized energies (blue lines) with respect to the Coulomb potential $-Ze/r$ (orange line). The eigenfunctions of the Hamiltonian with eigenvalue E_n are, see Eq. (4.152),

$$\varphi_{n,l,m}(\mathbf{r}) = R_{n,l}(r) Y_{l,m}(\theta, \phi). \tag{4.190}$$

These functions are also called **orbitals**. Since the integer m can take $2l + 1$ values, and $l = 0, 1, \dots, n-1$, the degeneracy D_n of the eigenvalue E_n is

$$D_n = \sum_{l=0}^{n-1}(2l+1) = 2\frac{n(n-1)}{2} + n = n^2. \tag{4.191}$$

A note on nomenclature. For small values of the angular momentum l, it is common to alternatively refer to orbitals as s if $l = 0$, p if $l = 1$, d if $l = 2$, and f if $l = 3$. Therefore, the ground state of the Hydrogen atom is also called the $1s$ state, the bound states of the second level are called $2s$ and $2p$ states, those of the third level are called $3s$, $3p$, and $3d$ states, and so on.

The results obtained in this section are of extraordinary importance. They demonstrate that quantum mechanics is capable of explaining one of the greatest myster-

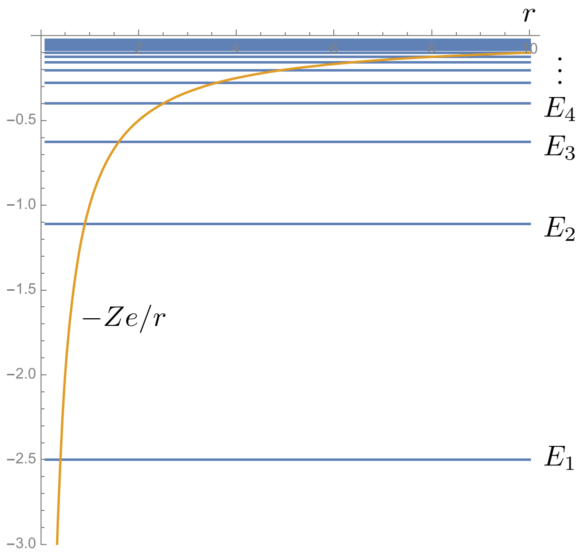

Fig. 4.2 Potential energy of a nucleus with charge Ze and position of discrete energy levels (eigenvalues)

ies of the universe, namely the stability of matter. Before the advent of quantum mechanics, it was not possible to explain even the stability of a simple system like the Hydrogen atom. Classically, the electron could not orbit indefinitely around the nucleus. Being a charged particle, it would radiate light due to its accelerated motion. Radiating light, it would lose energy until collapsing onto the nucleus. The quantum view of the universe does not use position and momentum to describe particles but wavefunctions. And if the electron is in an eigenfunction of the Hamiltonian, then the mean values of all observables are independent of time, see the discussion under Eq. (1.153). Therefore, everything is stationary, and there can be no radiation.

4.9.1 Semiclassical Derivation of Hydrogenoid Levels

Classically, an electron located at a distance r from a nucleus with charge Ze and having a speed with a magnitude of v possesses an energy

$$E = T + V = \frac{1}{2} m_e v^2 - \frac{Ze^2}{r}. \tag{4.192}$$

In order for the electron to orbit around the nucleus, the Coulomb attractive force $F_1 = Ze^2/r^2$ must be equal to the centrifugal force $F_2 = m_e v^2/r$. From this equality, it is immediately deduced that

$$m_e v^2 = \frac{Ze^2}{r}, \tag{4.193}$$

which inserted in Eq. (4.192) yields

$$E = -\frac{1}{2}\frac{Ze^2}{r}. \tag{4.194}$$

Now, let us assume that the angular momentum is quantized, meaning that $m_e v r = n\hbar$. It follows from Eq. (4.193) that

$$v^2 = \frac{Ze^2}{m_e r} = \frac{n^2\hbar^2}{m_e^2 r^2} \qquad \Rightarrow \qquad \frac{1}{r} = \frac{m_e Z e^2}{n^2 \hbar^2}. \tag{4.195}$$

Substitution in Eq. (4.194) gives

$$E = E_n = -\frac{m_e Z^2 e^4}{2n^2\hbar^2}. \tag{4.196}$$

which is identical to Eq. (4.188).

4.9.2 Radial Functions

We now want to take a closer look at the radial functions of the first atomic levels. We have

$$R_{n,l}(r) = \frac{\chi_{n,l}(r)}{r} = e^{-\kappa r} \sum_{q=0}^{n-l-1} c_q \, \kappa^{q+l+1} \, r^{q+l}. \tag{4.197}$$

Note that the coefficients c_q depend on n and l since they are determined by the recursive system in Eq. (4.185), where both l and n appear. Similarly, the coefficient κ depends on n as it is expressed in terms of $E = E_n$, thus

$$\kappa = \frac{\sqrt{2m_e |E_n|}}{\hbar} = \sqrt{\frac{2m_e^2 Z^2 e^4}{2n^2\hbar^2}}\frac{1}{\hbar} = \frac{m_e Z e^2}{n\hbar^2} = \frac{Z}{n a_{\mathrm{B}}}, \tag{4.198}$$

where we introduce the **Bohr radius**

$$a_{\mathrm{B}} \equiv \frac{\hbar^2}{m_e e^2} = 0.5 \times 10^{-10}\mathrm{m}. \tag{4.199}$$

Since κ appears in the exponential of the radial function, the Bohr radius gives us an estimate of how extended the radial function is. It is also observed that as n increases, and consequently, as the energy increases, the quantity κ decreases. This means that with increasing energy, the radial functions become more and more extended. Particularly transparent is the expression of atomic levels' energy in terms of the Bohr radius

$$E_n = -\frac{Z^2 e^2}{2 a_{\rm B} n^2}. \tag{4.200}$$

This is indeed the classical energy of an electron orbiting around a nucleus with charge Ze at the distance $n^2 a_{\rm B}/Z$, compared with Eq. (4.194).

For $n = 1$ the Eq. (4.197) yields

$$R_{1,0}(r) = c_0 \left(\frac{Z}{a_{\rm B}}\right) e^{-\frac{Zr}{a_{\rm B}}}. \tag{4.201}$$

We can determine the coefficient c_0 by imposing that the total wavefunction $\varphi_{n,l,m}$ is normalized to one. Since we have normalized the spherical harmonics to one, the normalization condition is

$$\begin{aligned} 1 = |c_0|^2 \left(\frac{Z}{a_{\rm B}}\right)^2 \int_0^\infty dr\, r^2 e^{-2\frac{Zr}{a_{\rm B}}} &= |c_0|^2 \frac{a_{\rm B}}{Z} \int_0^\infty dx\, x^2 e^{-2x} \\ &= \frac{|c_0|^2}{8} \frac{a_{\rm B}}{Z} \Gamma(3) = \frac{|c_0|^2}{4} \frac{a_{\rm B}}{Z}, \end{aligned} \tag{4.202}$$

where we have recognized the Euler Gamma function, see Appendix C. Therefore

$$R_{1,0}(r) = 2 \left(\frac{Z}{a_{\rm B}}\right)^{3/2} e^{-\frac{Zr}{a_{\rm B}}}. \tag{4.203}$$

So, the radial function of the ground state is a simple exponential, see Fig. 4.3.

We now consider the principal quantum number $n = 2$. In this case, we can have $l = 0$ or $l = 1$. For $l = 0$, the recursive system provides

$$c_1 = \frac{2-4}{2} c_0 = -c_0, \tag{4.204}$$

and therefore

$$R_{2,0}(r) = c_0 \left(\frac{Z}{2a_{\rm B}}\right) e^{-\frac{Zr}{2a_{\rm B}}} \left(1 - \frac{Zr}{2a_{\rm B}}\right). \tag{4.205}$$

As usual, the coefficient c_0 needs to be determined through normalization, and it is easy to demonstrate that $c_0 = \sqrt{2Z/a_{\rm B}}$. We can then write

$$R_{2,0}(r) = \left(\frac{Z}{2a_{\rm B}}\right)^{3/2} e^{-\frac{Zr}{2a_{\rm B}}} \left(2 - \frac{Zr}{a_{\rm B}}\right). \tag{4.206}$$

Note that this radial function has a zero at $r = 2a_{\rm B}/Z$. This means that there is a special distance from the origin where the probability of finding the electron is zero, see Fig. 4.3. For $l = 1$, the only nonzero coefficient is the first one, and therefore

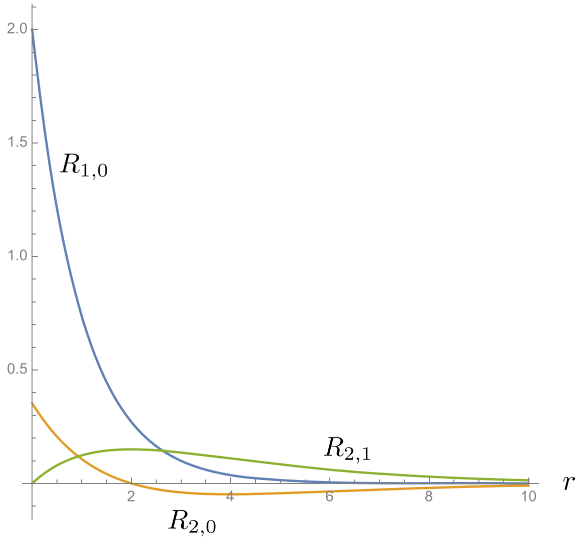

Fig. 4.3 Radial part of the eigenfunctions of an electron subjected to the potential of a charge Ze

$$R_{2,1}(r) = c_0 \left(\frac{Z}{2a_\mathrm{B}}\right)^2 e^{-\frac{Zr}{2a_\mathrm{B}}} r, \tag{4.207}$$

and from the normalization condition, it is easily found that $c_0 = \sqrt{2Z/(3a_\mathrm{B})}$. We can then write

$$R_{2,1}(r) = \left(\frac{Z}{2a_\mathrm{B}}\right)^{3/2} e^{-\frac{Zr}{2a_\mathrm{B}}} \frac{Zr}{\sqrt{3}\, a_\mathrm{B}}. \tag{4.208}$$

Similarly, it is possible to proceed to determine all the other radial functions. In Fig. 4.3, we show all the radial functions that we have just derived.

4.10 Exercises

1. Consider a particle of mass m and charge q bound to the $x - y$ plane in the presence of an electric field $\mathbf{E} = (-\frac{m\omega^2}{q}x, 0, 0)$ directed along the x axis and of a magnetic field $\mathbf{B} = (0, 0, B)$ directed along the z axis.
   i. Verify that the scalar potential $V = \frac{m\omega^2}{2q}x^2$ and the vector potential $\mathbf{A} = \frac{B}{2}(-y, x, 0)$ provide the electromagnetic fields mentioned above.
   ii. Write the Lagrangian of the problem and derive the Euler-Lagrange equations
   iii. Solve the Euler-Lagrange equations with initial conditions $x(0) = r$, $y(0) = 0$ and $\dot{x}(0) = 0$, $\dot{y}(0) = -\omega_B r$ with $\omega_B = \frac{qB}{mc}$ cyclotron frequency. What is the curve which describes the trajectory of the particle?

Solution *i. For the electric field we have* $E_x = -\frac{\partial}{\partial x} V = -\frac{m\omega^2}{q} x$, $E_y = -\frac{\partial}{\partial y} V = 0$, $E_z = -\frac{\partial}{\partial z} V = 0$, *while for the magnetic field we have* $B_x = \frac{\partial}{\partial y} A_z - \frac{\partial}{\partial z} A_x = 0$, $B_y = -\frac{\partial}{\partial x} A_z + \frac{\partial}{\partial z} A_x = 0$, $B_z = \frac{\partial}{\partial x} A_y - \frac{\partial}{\partial y} A_x = B$.
ii. The Lagrangian of the system is $L = \frac{m}{2}(\dot{x}^2 + \dot{y}^2) + \frac{1}{2}\omega_B(-\dot{x}y + \dot{y}x) - \frac{1}{2}m\omega^2 x^2$ *and therefore the Euler-Lagrange equations are*

$$\ddot{x} - \omega_B \dot{y} + \omega^2 x = 0, \qquad \ddot{y} + \omega_B \dot{x} = 0.$$

iii. By differentiating the first equation and substituting $\ddot{y}$ *for the value obtainable from the second equation we obtain an equation for* $v_x = \dot{x}$ *of the form of a harmonic oscillator, that is* $\ddot{v}_x + \Omega^2 v_x = 0$, with $\Omega^2 = \omega_B^2 + \omega^2$. *The most general solution is* $v_x(t) = \alpha \cos \Omega t + \beta \sin \Omega t$ *and taking account that* $v_x(0) = 0$ *it must be* $\alpha = 0$. *To calculate* β *it is necessary to determine* $\dot{v}_x(0) = \ddot{x}(0) = \omega_B \dot{y}(0) - \omega^2 x(0) = -\omega_B^2 r - \omega^2 r = -\Omega^2 r$ and therefore $\beta = -\Omega r$. *It follows that* $x(t) = r + \int_0^t v_x(t')dt' = r \cos \Omega t$ while $\dot{y}(t) = \dot{y}(0) - \omega_B(x(t) - x(0)) = -\omega_B r - \omega_B r(\cos \Omega t - 1) = -\omega_B r \cos \Omega t$ *from which it follows that* $y(t) = -\frac{\omega_B}{\Omega} r \cos \Omega t$. *The trajectory is therefore an ellipse.*

2. Determine the wavefunction of a particle of mass m e charge q constrained to move along the x axis knowing that at a distance R from the x axis the electric field is zero and the magnetic field is B. Also determine the average kinetic energy of the particle as B grows.
   Hint: Use Ampere's law

   $$\oint \mathbf{B} \cdot d\mathbf{l} = \frac{4\pi}{c} J$$

   where J is the current density associated with the particle.
   Solution *From Ampere's law we find* $J = \frac{c}{2} RB$. *On the other hand the current density associated with a generic wavefunction* $\psi(x) = \rho(x) \exp[i\theta(x)]$ is $J = \frac{q\hbar}{m}\rho^2 \partial_x \theta$. *It follows that* $\rho = 1/\sqrt{L}$ *(with L the wire length)* and $\theta = \left(\frac{mcRBL}{2q\hbar}\right) x$. *The wave function is therefore a plane wave and the average value of the kinetic energy is* $\langle T \rangle = \frac{m}{8}\left(\frac{cRBL}{q}\right)^2$.
3. A particle of mass m in two dimensions is described by the Hamiltonian $\hat{H} = \frac{1}{2m}(\hat{p}_x^2 + \hat{p}_y^2) + V_1(\hat{x}) + V_2(\hat{y})$ where $V_1(x) = -\sqrt{\frac{\hbar^3\omega}{m}}\delta(x)$ and $V_2(y) = \frac{1}{2}m\omega^2 y^2$.
   i. Calculate the energy E_0 and the wavefunction $\psi_0(x, y)$ normalized to 1 of the ground state.
   ii. Calculate the average value of the operators $\hat{x}\hat{y}^2$, $\hat{x}^2\hat{y}$ and $\hat{x}^2\hat{y}^2$ on ground state.
   Solution *i. Since the Hamiltonian is separable the eigenvalues are the sum of the eigenvalues of the Hamiltonians along the x and y directions. As the ground state is requested, we look for the ground states of* $\hat{H}_1 = \frac{1}{2m}\hat{p}_x^2 + V_1(\hat{x})$ *and* $\hat{H}_2 = \frac{1}{2m}\hat{p}_y^2 + V_2(\hat{y})$. *The ground state of* $\hat{H}_1$ *is the bound state* $\psi_{1,0}(x) = \sqrt{k}\, e^{-k|x|}$

with $k = \sqrt{\frac{m\omega}{\hbar}}$ *and has energy* $E_{1,0} = -\frac{1}{2}\hbar\omega$. *The Hamiltonian along the direction y is that of a harmonic oscillator of frequency* ω *for which the ground state is* $\psi_{2,0}(y) = (\frac{k^2}{\pi})^{1/4}\, e^{-k^2x^2/2}$ *and has energy* $E_{2,0} = \frac{1}{2}\hbar\omega$. *We conclude that energy of the ground state of* $\hat{H}$ is $E_0 = E_{1,0} + E_{2,0} = 0$ *and that the wavefunction normalized to 1 of the ground state of* $\hat{H}$ *is*

$$\psi_0(x, y) = \frac{k}{\pi^{1/4}}\, e^{-k|x| - k^2y^2/2}$$

ii. The ground state wavefunction is even along x and y, *therefore the average value of the operators* $\hat{x}\hat{y}^2$ *and* $\hat{x}^2\hat{y}$ *is null. The average value of* $\hat{x}^2\hat{y}^2$ *is given by*

$$\langle \hat{x}^2\hat{y}^2\rangle = \frac{k^2}{\sqrt{\pi}} \int_{-\infty}^{\infty} dx\; x^2 e^{-2k|x|} \int_{-\infty}^{\infty} dy\; y^2 e^{-k^2y^2} = \frac{k^2}{\sqrt{\pi}} \frac{1}{2k^3} \frac{\sqrt{\pi}}{2k^3} = \frac{1}{4k^4} = \frac{\hbar^2}{4m^2\omega^2}.$$

4. Consider a quantum harmonic oscillator in two dimensions with Hamiltonian

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{\hat{p}_y^2}{2m} + \frac{1}{2}m\omega^2(\hat{x}^2 + \hat{y}^2)$$

Knowing that a measurement of energy always provides the value $2\hbar\omega$, determine the normalized state $|\Psi\rangle$ of the particle from the knowledge of the following average values:

$$\langle\Psi|\hat{x}^2|\Psi\rangle = \frac{\hbar}{m\omega}, \qquad \langle\Psi|\hat{x}\hat{y}|\Psi\rangle = -\frac{\hbar}{2\sqrt{2}\,m\omega}$$

Solution *From the energy information we can write that* $|\Psi\rangle = \alpha|10\rangle + \beta|01\rangle$ *where* $|n_x n_y\rangle$ *are the eigenkets of* $\hat{H}$ *with eigenvalue* $\hbar\omega(n_x + n_y + 1)$. *The normalization tells us that* $|\alpha|^2 + |\beta|^2 = 1$. *From the first average value we deduce that*

$$\frac{\hbar}{m\omega} = \frac{\hbar}{m\omega}\left(\frac{3}{2}|\alpha|^2 + \frac{1}{2}|\beta|^2\right)$$

hence $3|\alpha|^2 + |\beta|^2 = 2$. *Using the condition on the norm we get* $|\alpha|^2 = |\beta|^2 = 1/2$. *Since the state is defined up to an overall phase we can choose real* α *and write* $|\Psi\rangle = \frac{1}{\sqrt{2}}(|10\rangle + e^{i\theta}|01\rangle)$. *To obtain the* θ *phase we use the last information:*

$$-\frac{\hbar}{2\sqrt{2}\,m\omega} = \frac{1}{2}\left(\langle 10| + e^{-i\theta}\langle 01|\right)\hat{x}\hat{y}\left(|10\rangle + e^{i\theta}|01\rangle\right) = \frac{\hbar}{2m\omega}\cos\theta$$

from which it follows that $\theta = -\pi/4$.

5. Indicating with $\hat{p}_x$ and $\hat{p}_y$ the momentum operators along the x and y directions and with $\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$ the angular momentum operator along the z direction
i. Calculate the commutators $C_1 = [\hat{p}_x^2 + \hat{p}_y^2, \hat{L}_z]$ and $C_2 = [\hat{x}^2 + \hat{y}^2, \hat{L}_z]$
ii. Consider an isotropic harmonic oscillator in two dimensions of Hamiltonian $\hat{H} = \hbar\omega(\hat{a}_x^\dagger \hat{a}_x + \hat{a}_y^\dagger \hat{a}_y + 1)$ with $\hat{a}_x = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + \mathrm{i}\frac{\hat{p}_x}{sqrt2m\hbar\omega}$ and $\hat{a}_y = \sqrt{\frac{m\omega}{2\hbar}}\hat{y} + \mathrm{i}\frac{\hat{p}_y}{sqrt2m\hbar\omega}$ the lowering operators along the x and y directions. Is it possible to find simultaneous eigenkets of $\hat{H}$ and $\hat{L}_z$?
iii. In the case of an affirmative answer to the previous point, if a simultaneous autoket has eigenvalue $2\hbar\omega$ for $\hat{H}$ which eigenvalue can have for $\hat{L}_z$?
Solution *i. We have*

$$C_1 = [\hat{p}_x^2 + \hat{p}_y^2, \hat{x}\hat{p}_y - \hat{y}\hat{p}_x] = [\hat{p}_x^2, \hat{x}]\hat{p}_y - [\hat{p}_y^2, \hat{y}]\hat{p}_x = 2\hat{p}_x[\hat{p}_x, \hat{x}]\hat{p}_y - 2\hat{p}_y[\hat{p}_y, \hat{y}]\hat{p}_x$$
$$= -2\mathrm{i}\hbar(\hat{p}_x\hat{p}_y - \hat{p}_y\hat{p}_x) = 0$$

$$C_2 = [\hat{x}^2 + \hat{y}^2, \hat{x}\hat{p}_y - \hat{y}\hat{p}_x] = -\hat{y}[\hat{x}^2, \hat{p}_x] + \hat{x}[\hat{y}^2, \hat{p}_y] = -2\hat{y}\hat{x}[\hat{x}, \hat{p}_x] + 2\hat{x}\hat{y}[\hat{y}, \hat{p}_y]$$
$$= -2\mathrm{i}\hbar(\hat{y}\hat{x} - \hat{x}\hat{y}) = 0$$

ii. The Hamiltonian can be rewritten as $\hat{H} = \frac{1}{2m}(\hat{p}_x^2 + \hat{p}_y^2) + \frac{1}{2}m\omega^2(\hat{x}^2 + \hat{y}^2)$. *Since both the kinetic and potential parts commute with* $\hat{L}_z$ *we have* $[\hat{H}, \hat{L}_z] = 0$. *It follows that* $\hat{H}$ *and* $\hat{L}_z$ *admit simultaneous eigenkets.*
iii. The eigenkets of $\hat{H}$ *are given by* $|n_x n_y\rangle = \frac{(\hat{a}_x^\dagger)^{n_x}}{\sqrt{n_x!}}\frac{(\hat{a}_y^\dagger)^{n_y}}{\sqrt{n_y!}}|00\rangle$ *and have eigenvalue* $\hbar\omega(n_x + n_y + 1)$. *So the autokets of* $\hat{H}$ *with eigenvalue* $2\hbar\omega$ *are* $|10\rangle$ and $|01\rangle$. *From the previous point we know that starting from these two kets it must be possible to construct two eigenkets of* $\hat{L}_z$. *The required eigenvalues are therefore given by the eigenvalues of the matrix*

$$\mathbb{L}_z = \begin{pmatrix} \langle 10|\hat{L}_z|10\rangle & \langle 10|\hat{L}_z|01\rangle \\ \langle 01|\hat{L}_z|10\rangle & \langle 01|\hat{L}_z|01\rangle \end{pmatrix}$$

Expressing the operators $\hat{x}$, $\hat{y}$ and $\hat{p}_x$, $\hat{p}_y$ *in terms of the lowering operators e elevation is found* $\hat{L}_z = \frac{\hbar}{2\mathrm{i}}[(\hat{a}_x + \hat{a}_x^\dagger)(\hat{a}_y - \hat{a}_y^\dagger) - (\hat{a}_y + \hat{a}_y^\dagger)(\hat{a}_x - \hat{a}_x^\dagger)]$ *from which immediately follows that* $\mathbb{L}_z = \hbar\sigma_y$ with σ_y *the Pauli matrix along the y direction. So the simultaneous eigenkets that have eigenvalue* $2\hbar\omega$ for $\hat{H}$ *have eigenvalues* $\pm\hbar$ for $\hat{L}_z$.

6. The Hamiltonian for a particle of mass m in three dimensions is that of the isotropic harmonic oscillator

$$\hat{H} = \frac{1}{2m}(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) + \frac{1}{2}m\omega^2(\hat{x}^2 + \hat{y}^2 + \hat{z}^2).$$

Denoting with $|n_x, n_y, n_z\rangle$ the eigenkets of $\hat{H}$ the particle is found in the state $|\Psi\rangle = \frac{1}{\sqrt{2}}\big(|1, 0, 0\rangle + e^{\mathrm{i}\alpha}|0, 1, 0\rangle\big)$ with $\alpha \in (0, 2\pi)$. Calculate α knowing that the average value of the angular momentum along the z axis is equal to $\hbar$.
Solution *The wavefunction is given by*

$$\begin{aligned}\Psi(\mathbf{r}) = \langle \mathbf{r}|\Psi\rangle &= \frac{1}{\sqrt{2}}\big(\Psi_1(x)\Psi_0(y)\Psi_0(z) + e^{\mathrm{i}\alpha}\Psi_0(x)\Psi_1(y)\; Q_0(z)\big)\\ &= \frac{1}{2}\Big(\frac{m\omega}{\pi\hbar}\Big)^{3/4} 2\frac{x + e^{\mathrm{i}\alpha}y}{x_0} e^{-\frac{x^2+y^2+z^2}{2x_0^2}},\end{aligned}$$

In polar coordinates $x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$ *and* $r^2 = x^2 + y^2 + z^2$. *Then set* $\bar{r} \equiv r/x_0$ *we can rewrite the wave function as*

$$\begin{aligned}\Psi(\mathbf{r}) &= \Big(\frac{m\omega}{\pi\hbar}\Big)^{3/4}\big[\cos\phi + e^{\mathrm{i}\alpha}\sin\phi\big]\sin\theta \times \bar{r}e^{-\bar{r}^2/2}\\ &= \Big(\frac{m\omega}{\pi\hbar}\Big)^{3/4}\big[\big(\frac{1 - \mathrm{i}e^{\mathrm{i}\alpha}}{2}\big)e^{\mathrm{i}\phi} + \big(\frac{1 + \mathrm{i}e^{\mathrm{i}\alpha}}{2}\big)e^{-\mathrm{i}\phi}\big]\sin\theta \times \bar{r}e^{-\bar{r}^2/2}\\ &= \Big(\frac{m\omega}{\pi\hbar}\Big)^{3/4}\sqrt{\frac{8\pi}{3}}\big[\big(\frac{1 - \mathrm{i}e^{\mathrm{i}\alpha}}{2}\big)Y_{1,1}(\theta, \phi) + \big(\frac{1 + \mathrm{i}e^{\mathrm{i}\alpha}}{2}\big)Y_{1,-1}(\theta, \phi)\big] \times \bar{r}e^{-\bar{r}^2/2}\end{aligned}$$

The required expectation value is therefore

$$\begin{aligned}\langle\Psi|\hat{L}_z|\Psi\rangle = \int d\mathbf{r}\langle\Psi|\mathbf{r}\rangle\langle\mathbf{r}|\hat{L}_z|\Psi\rangle &= -\mathrm{i}\hbar\int d\mathbf{r}\langle\Psi|\mathbf{r}\rangle\frac{\partial}{\partial\phi}\langle\mathbf{r}|\Psi\rangle\\ &= \hbar\Big(\frac{m\omega}{\pi\hbar}\Big)^{3/2}\frac{8\pi}{3}\big[\big|\frac{1 - \mathrm{i}e^{\mathrm{i}\alpha}}{2}\big|^2 - \big|\frac{1 + \mathrm{i}e^{\mathrm{i}\alpha}}{2}\big|^2\int dr\, r^2\bar{r}^2e^{-\bar{r}^2}\big]\\ &= \hbar\frac{8}{3\sqrt{\pi}}\sin\alpha\int d\bar{r}\,\bar{r}^4e^{-\bar{r}^2} = \hbar\sin\alpha\end{aligned}$$

For the average value to be $\hbar$ *it must be* $\alpha = \pi/2$.

7. A particle bound to a sphere of unit radius is described by the wavefunction $\Psi(\theta, \phi) = C(1 + \mathrm{i}\cos\theta)$. Calculate
i. The normalization constant C such that $\int d\Omega|\Psi(\theta, \phi)|^2 = 1$
ii. The probability that a measure of angular momentum along the z axis provides 0
iii. The probability that a measure of the square of the angular momentum provides 0
iv. The probability that a measure of the angular momentum along the x axis provides $\hbar$
Solution *The given wavefunction can be rewritten as* $\Psi = C\sqrt{4\pi}\,(Y_{0,0} + \frac{\mathrm{i}}{\sqrt{3}}Y_{1,0})$
i. Taking into account that spherical harmonics are orthonormal the constant C must satisfy $|C|^2 4\pi(1 + \frac{1}{3}) = 1$ *hence* $C = \sqrt{\frac{3}{16\pi}}$.
ii. The required probability is given by $P(L_z = 0) = \sum_{l=0}^{\infty}\big|\int d\Omega\, Y_{l,0}^*(\theta, \phi)$

$\Psi(\theta,\phi)\big|^2 = 1$. *Alternatively, this result can be deduced from the fact that* Ψ *is an eigenfunction of* L_z *with zero eigenvalue.*
iii. The required probability is given by $P(L^2=0) = \big|\int d\Omega\, Y^*_{0,0}(\theta,\phi)\,\Psi(\theta,\phi)\big|^2 = 3/4$.
iv. Denoting with $Y^{(x)}_{l,m}(\theta,\phi)$ *the eigenfunctions of* L_x *the required probability is given by*

$$P(L_x=1) = \sum_{l=1}^{\infty} \Big|\int d\Omega\, Y^{(x)*}_{l,1}(\theta,\phi)\Psi(\theta,\phi)\Big|^2 = \frac{1}{4}\int d\Omega \big|Y^{(x)*}_{1,1}(\theta,\phi)Y_{1,0}(\theta,\phi)\big|^2.$$

The matrix that represents L_x *in the space with* $l=1$ *and given by* $L_x = \frac{\hbar}{\sqrt{2}}\begin{pmatrix}0&1&0\\1&0&1\\0&1&0\end{pmatrix}$ *and the eigenvector with eigenvalue* $\hbar$ *is* $(\frac{1}{2},\frac{1}{\sqrt{2}},\frac{1}{2})$, *from which* $Y^{(x)}_{1,1} = \frac{1}{2}Y_{1,1} + \frac{1}{\sqrt{2}}Y_{1,0} + \frac{1}{2}Y_{1,-1}$. *It follows that* $P(L_x=1) = 1/8$.

8. For two generic Hermitian operators $\hat{A}$ and $\hat{B}$ the Heisenberg uncertainty principle establishes that $\langle\hat{\sigma}^2_A\rangle\langle\hat{\sigma}^2_B\rangle \geq \frac{1}{4}|\langle[\hat{A},\hat{B}]\rangle|^2$. Check this principle in the case where $\hat{A}=\hat{L}_x$, $\hat{B}=\hat{L}_y$ and the system state is $|\psi\rangle = \frac{1}{\sqrt{2}}(|1,1\rangle + |1,-1\rangle)$.
   Solution *We have* $\hat{L}_x = \frac{1}{2}(\hat{L}_+ + \hat{L}_-)$ *and* $\hat{L}_y = \frac{1}{2i}(\hat{L}_+ - \hat{L}_-)$. *So* $\hat{L}_x|\psi\rangle = \hbar|1,0\rangle$ *and* $\hat{L}_y|\psi\rangle = |\emptyset\rangle$. *From this last identity we infer that* $\langle\hat{L}_y\rangle = \langle\hat{L}^2_y\rangle = 0$ *and therefore* $\langle\hat{\sigma}^2_{L_x}\rangle\langle\hat{\sigma}^2_{L_y}\rangle = 0$. *Furthermore* $\langle[\hat{L}_x,\hat{L}_y]\rangle = \langle\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x\rangle = 0$. *Being* $0 \geq 0$ *the Heisenberg principle is satisfied.*

More Exercises

9. Calculate the triple commutator

$$[[[\hat{p}_x, \hat{L}_y], \hat{L}_x], \hat{y}]$$

10. A particle in three dimensions is described by the Hamiltonian $\hat{H} = \alpha\hat{L}^2_z + \hat{V}$, where

$$\langle\mathbf{r}|\hat{V}|\Psi\rangle = \frac{2\alpha\hbar^2}{\phi(\phi-2\pi)}\langle\mathbf{r}|\Psi\rangle$$

   for any ket $|\Psi\rangle$.
   i. Find the dependence on ϕ of the eigenfunction of $\hat{H}$ with zero energy (Hint: Write this eigenfunction as a polynomial of degree 2 in ϕ)
   ii. Normalize the eigenfunction of the previous point to 1
   iii. Calculate the average value of the angle ϕ.
11. A particle in three dimensions is described by the Hamiltonian $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{\mathbf{r}})$ where the potential $V(\mathbf{r})$ depends only on the modulus $r = |\mathbf{r}|$ and holds

$$V(\mathbf{r}) = \begin{cases} 0 & r < R \\ \infty & r > R \end{cases}$$

So the potential describes a potential well of spherical symmetry with infinitely high walls. Calculate eigenvalues and eigenfunctions of $\hat{H}$ in the subspace of wavefunctions with zero angular momentum.

12. A particle in three dimensions is described by the Hamiltonian $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{r}^2$. Determine eigenfunctions, eigenvalues and their degeneracy. (Hint: Write $\hat{p}^2 = \hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2$ e $\hat{r}^2 = \hat{x}^2 + \hat{y}^2 + \hat{z}^2$ and use raising and lowering operators for each direction).
13. A particle in three dimensions is described by the Hamiltonian $\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(\hat{\mathbf{r}})$ where the potential $V(\mathbf{r})$ is given by

    $$V(\mathbf{r}) = \begin{cases} 0 & |x| < a, |y| < b, z \in (0, c) \\ \infty & \text{otherwise} \end{cases}$$

    Determine eigenfunctions, eigenvalues and their degeneracy.
14. A particle of mass m and charge $Q > 0$ in three dimensions is subject to the scalar potential $\phi(\mathbf{r}) = \frac{1}{2Q}m\omega^2 z^2$, with $\omega = \frac{QB}{2mc}$, and vector potential $\mathbf{A}(\mathbf{r}) = \frac{B}{2}(-y, x, 0)$. Calculate the eigenfunction and the eigenvalue of the ground state.
15. A particle of mass m in two dimensions is described by the Hamiltonian

    $$\hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{\hat{p}_y^2}{2m} + \frac{1}{2}m\omega_x^2\hat{x}^2 + \frac{1}{2}m\omega_y^2\hat{y}^2$$

    where p_x and p_y are the conjugate moments of x and y. Defining the raising and lowering operators for each direction determine eigenkets and eigenvalues of $\hat{H}$.
16. A particle of mass m in three dimensions is subject to the potential

    $$V(\mathbf{r}) = -a[\delta(x) + \delta(y) + \delta(z)].$$

    Determine the eigenfunction and eigenvalue of the ground state.
17. A particle of mass m in three dimensions is subject to the spherically symmetric potential

    $$V(\mathbf{r}) = \begin{cases} 0 & R_1 < r < R_2 \\ \infty & \text{otherwise} \end{cases}$$

    Determine eigenfunctions and eigenvalues with orbital angular momentum $l = 0$.

18. An electron of a Hydrogen atom is found in the ground state. Calculate the average value of the electron-proton force $F = \frac{e^2}{r^2}$ and the potential energy $V = -\frac{e^2}{r}$.
19. Consider a particle in three dimensions whose angular part is described by the ket $|l, m\rangle$. Calculate the variance of the angular momentum operators $\hat{L}_x$ and $\hat{L}_y$ along the x and y directions.

Chapter 5
Spin and Addition of Angular Momenta

5.1 Spin

In this section, we discover that elementary particles, such as electrons or quarks, possess internal degrees of freedom. In other words, a wavefunction alone is no longer sufficient to describe them.

Let us consider again the hydrogen atom ($Z = 1$) from the previous chapter and immerse it in a spatially uniform magnetic field **B**. As we know, due to the presence of the magnetic field, the Hamiltonian changes. In Eq. (4.60), we precisely derived the form of the Hamiltonian that suits our case, i.e., that of a particle exposed to a uniform magnetic field. We rewrite it here for convenience

$$\hat{H} = \frac{\hat{p}^2}{2m} - \frac{Q}{2mc}(\hat{\mathbf{r}} \times \hat{\mathbf{p}})\cdot\mathbf{B} + \frac{Q^2}{8mc^2}(\hat{r}^2 B^2 - (\hat{\mathbf{r}} \cdot \mathbf{B})^2) + Q\phi(\hat{\mathbf{r}}, t). \tag{5.1}$$

To calculate the new eigenvalues and eigenvectors, we need to solve $\hat{H}|E, k\rangle = E|E, k\rangle$ with $\phi(\mathbf{r}) = e/r$ being the Coulomb (central) potential, $Q = -e$ the charge of the electron, and $m = m_e$ the electron's mass. For a sufficiently small magnetic field, we can neglect the quadratic terms in B. Remembering that $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$, the eigenvalue equation becomes

$$\left(\hat{H}_0 + \frac{e}{2m_e c}\mathbf{B}\cdot\hat{\mathbf{L}}\right)|E, k\rangle = E|E, k\rangle, \tag{5.2}$$

where we have defined $\hat{H}_0$ as the Hamiltonian of the hydrogen atom without a magnetic field.

$$\hat{H}_0 \equiv \frac{\hat{p}^2}{2m_e} - e\phi(\hat{r}). \tag{5.3}$$

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Let us choose the magnetic field oriented along the z direction: $\mathbf{B} = (0, 0, B)$. In this case, the dot product $\hat{\mathbf{L}} \cdot \mathbf{B} = B\hat{L}_z$. Multiplying Eq. (5.2) by the bra $\langle \mathbf{r}|$ and expressing the Laplacian in polar coordinates, see Eq. (4.150), we obtain the eigenvalue equation for the wave function $\varphi_{E,k}(\mathbf{r}) = \langle \mathbf{r}|E, k\rangle$:

$$\left(-\frac{\hbar^2}{2m_e}\frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{\hbar^2}{2m_e r^2}\nabla^2_\Omega - \frac{e^2}{r} - \frac{eB}{2m_e c}i\hbar\frac{\partial}{\partial\phi}\right)\varphi_{E,k}(\mathbf{r}) = E\varphi_{E,k}(\mathbf{r}). \tag{5.4}$$

In obtaining this equation, we also use Eq. (4.102). If the magnetic field were zero, this would be precisely the eigenvalue equation for the hydrogen atom, which, as we know from Sect. 4.9, has eigenvalues $E_n = -e^2/(2a_{\mathrm{B}}n^2)$ and eigenfunctions $\varphi_{n,l,m}(\mathbf{r})$:

$$\left(-\frac{\hbar^2}{2m_e}\frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{\hbar^2}{2m_e r^2}\nabla^2_\Omega - \frac{e^2}{r}\right)\varphi_{n,l,m}(\mathbf{r}) = E_n\varphi_{n,l,m}(\mathbf{r}). \tag{5.5}$$

Now, the point is that the functions $\varphi_{n,l,m}(\mathbf{r}) = R_{n,l}(r)Y_{l,m}(\theta, \phi)$ continue to be eigenfunctions even in the presence of the magnetic field, as, according to Eq. (4.115),

$$-\mathrm{i}\hbar\frac{\partial}{\partial\phi}\varphi_{n,l,m}(\mathbf{r}) = R_{n,l}(r)\left(-\mathrm{i}\hbar\frac{\partial}{\partial\phi}Y_{l,m}(\theta, \phi)\right) = m\hbar R_{n,l}(r)Y_{l,m}(\theta, \phi) = m\hbar\varphi_{n,l,m}(\mathbf{r}). \tag{5.6}$$

Hence

$$\left(-\frac{\hbar^2}{2m_e}\frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{\hbar^2}{2m_e r^2}\nabla^2_\Omega - \frac{e^2}{r} - \frac{eB}{2m_e c}\mathrm{i}\hbar\frac{\partial}{\partial\phi}\right)\varphi_{n,l,m}(\mathbf{r}) = \left(E_n + \frac{e\hbar B}{2m_e c}m\right)\varphi_{n,l,m}(\mathbf{r}). \tag{5.7}$$

Therefore, a weak uniform magnetic field does not change the eigenfunctions $\varphi_{n,l,m}$ of the hydrogen atom but alters the associated eigenvalues. The new eigenvalues are, in fact,

$$\tilde{E}_{n,m} = E_n + \frac{e\hbar B}{2m_e c}m \tag{5.8}$$

and depend not only on the principal quantum number n but also on the azimuthal quantum number m. This result can be derived in a couple of lines without resorting to the position representation. Let $|n, l, m\rangle$ be the ket whose inner product with the bra $\langle\mathbf{r}|$ yields the eigenfunction of the hydrogen atom

$$\varphi_{n,l,m}(\mathbf{r}) = \langle\mathbf{r}|n, l, m\rangle. \tag{5.9}$$

The kets $|n, l, m\rangle$ are therefore the eigenkets of $\hat{H}_0$ in Eq. (5.3)

$$\hat{H}_0|n, l, m\rangle = E_n|n, l, m\rangle. \tag{5.10}$$

The reader can easily verify that by multiplying this equation by the bra $\langle \mathbf{r}|$, we recover Eq. (5.5). They are also eigenkets of $\hat{L}_z$ with eigenvalue $\hbar m$. Therefore

$$\begin{aligned}\left(\hat{H}_0 + \frac{eB}{2m_e c}\hat{L}_z\right)|n, l, m\rangle &= \hat{H}_0|n, l, m\rangle + \frac{eB}{2m_e c}\hat{L}_z|n, l, m\rangle \\ &= \left(E_n + \frac{e\hbar B}{2m_e c}m\right)|n, l, m\rangle. \qquad (5.11)\end{aligned}$$

It is straightforward to verify that by multiplying this equation by the bra $\langle \mathbf{r}|$, we recover Eq. (5.7).

The quantity

$$\mu_{\mathrm{B}} \equiv \frac{e\hbar}{2m_e c} = 5.788 \times 10^{-5}\ \mathrm{eV/T} \qquad (5.12)$$

is called the **Bohr magneton** and has the physical dimensions of a magnetic moment. The correction to the energies of the hydrogen atom is, therefore, very transparent. Classically, a magnetic moment $\boldsymbol{\mu}$ in a magnetic field $\mathbf{B}$ has an energy equal to $-\boldsymbol{\mu} \cdot \mathbf{B}$. If the magnetic moment is generated by a loop of radius r located in the xy plane and carrying a current I, then $\boldsymbol{\mu} = (0, 0, \mu)$ is directed along the z axis and, along this axis, has a projection

$$\mu = \frac{I\pi r^2}{c}. \qquad (5.13)$$

If there is only one electron moving at a speed v in the loop, then the current it generates is

$$I = -\frac{ev}{2\pi r}. \qquad (5.14)$$

Substituting this expression into Eq. (5.13), we find the magnetic moment associated with an electron moving in a circular trajectory

$$\mu = -\frac{erv}{2c} = -\frac{eL_z}{2m_e c}, \qquad (5.15)$$

where $L_z = m_e r v$ is the angular momentum of the electron. If the value of this angular momentum is $L_z = \hbar m$, then the magnetic moment of the loop becomes

$$\mu = -\frac{e\hbar m}{2m_e c} = -\mu_{\mathrm{B}} m \qquad (5.16)$$

and the classical energy $-\mu B$ precisely coincides with the second term of Eq. (5.8).

The energy of the electron in the hydrogen atom can be experimentally measured. By conducting the experiment in the presence of a uniform magnetic field, we can verify whether the theoretical prediction is in agreement with the experiment. What happens is that there is a discrepancy. In particular, the theory predicts that if the electron is in the ground state $|1, 0, 0\rangle$ in the absence of a magnetic field, then as

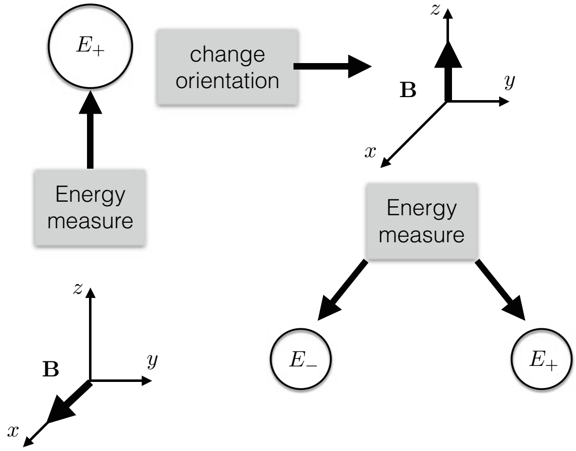

Fig. 5.1 The measurement of the energy of an electron subjected to a magnetic field directed along x yields the value E_+. Following a sudden change in the direction of the magnetic field from x to z, the energy measurement yields either E_+ or E_- with equal probabilities

B increases, its energy remains the same since, according to Eq. (5.8), $\tilde{E}_{1,0} = E_1$ is independent of B. Experimentally, however, it is found that as B increases, the energy level splits into two energy levels

$$E_+ = E_1 + \mu_B B, \qquad E_- = E_1 - \mu_B B \tag{5.17}$$

What is happening? It is happening that the quantum numbers $(n, l, m) = (1, 0, 0)$ are not sufficient to uniquely determine the state in which the electron can be found. Indeed, let us recall that according to the second postulate, if we measured E_+ then the electron would collapse into a state which, according to the third postulate, is orthogonal to the state in which it would collapse if we measured E_- (the eigenkets of an observable, such as the Hamiltonian, are mutually orthogonal if the associated eigenvalues are distinct). As often happens in the quantum world, the strangeness does not end here. Suppose we orient the magnetic field along x. Obviously, the z direction is nothing special, so if we repeated the same experiment, we would still measure the energies E_+ and E_-. However, this time, the states into which the electron collapses are not the same as before! In fact, what is experimentally found is that if we measure, for example, E_+ and then suddenly change the orientation of the magnetic field from the x axis to the z axis, see Fig. 5.1, then a subsequent energy measurement would yield the value E_+ with a probability of $1/2$ and the value E_- with a probability of $1/2$. From other experiments of this kind, it has been realized that the electron possesses, in addition to the "spatial" degrees of freedom, also an *internal degree of freedom*. Furthermore, it has been understood that all experimental results can be explained by adding, "by hand", to the Hamiltonian $\hat{H}_0$ an operator that acts exclusively on the internal degree of freedom.[1]

The operator to be added "by hand" is the following

---

[1] The term that we will add"by hand" actually comes from an even more fundamental equation than Schrödinger's, which we do not have the opportunity to address in this book.

$$\frac{e}{m_e c}\mathbf{B}\cdot\hat{\mathbf{S}}, \tag{5.18}$$

where the vector of operators $\hat{\mathbf{S}} = (\hat{S}_x, \hat{S}_y, \hat{S}_z) = (\hat{S}_1, \hat{S}_2, \hat{S}_3)$ satisfies the same commutation rules as the angular momentum operators, namely,

$$[\hat{S}_i, \hat{S}_j] = \mathrm{i}\hbar \sum_k \varepsilon_{ijk}\hat{S}_k, \tag{5.19}$$

compare with Eq. (4.66). Moreover, the only possible eigenvalue of the square operator $\hat{S}^2$ is $\hbar^2 3/4 = \hbar^2 \frac{1}{2}(\frac{1}{2}+1)$. Therefore, the internal degree of freedom is quantized and exists in a two-dimensional Hilbert space. In fact, for eigenvalues of $\hat{S}^2$ equal to $\hbar^2 3/4$, we have denoted with $|\frac{1}{2}, \frac{1}{2}\rangle$ and $|\frac{1}{2}, -\frac{1}{2}\rangle$ the only two simultaneous eigenkets of $\hat{S}^2$ and $\hat{S}_z$, see Sect. 4.6. However, since the electron also has spatial degrees of freedom, we necessarily need to complicate the notation. For example, we can denote with

$$|\mathbf{r}; \frac{1}{2}, m_s\rangle, \qquad m_s = \frac{1}{2}, -\frac{1}{2} \tag{5.20}$$

the state into which the electron collapses when a position measurement yields $\mathbf{r}$ and a measurement of $\hat{S}_z$ yields $\hbar m_s$. Similarly, we can indicate with

$$|n, l, m; \frac{1}{2}, m_s\rangle, \tag{5.21}$$

the state into which the electron collapses when an energy measurement yields E_n, a measurement of $\hat{L}^2$ yields $\hbar^2 l(l+1)$, a measurement of $\hat{L}_z$ yields $\hbar m$, and a measurement of $\hat{S}_z$ yields $\hbar m_s$. The operators $\hat{S}_i$, called **spin operators**, act only on the index m_s, while the "spatial" operators such as $\hat{\mathbf{r}}$, $\hat{\mathbf{p}}$, $\hat{\mathbf{L}}$ act, as before, only on the indices n, l, m. Particles with internal degrees of freedom like the electron are called **particles with spin** s, where s refers to the half-integer eigenvalue $\hbar^2 s(s+1)$ of $\hat{S}^2$. In the case of the electron, $s = \frac{1}{2}$, and thus, the electron is a spin-1/2 particle.

Let us see how adding the term in Eq. (5.18) allows us to explain the experimental results. The new Hamiltonian is the sum of the Hamiltonian in Eq. (5.2) and the new term in Eq. (5.18):

$$\hat{H} = \hat{H}_0 + \frac{e}{2m_e c}\mathbf{B}\cdot\hat{\mathbf{L}} + \frac{e}{m_e c}\mathbf{B}\cdot\hat{\mathbf{S}}. \tag{5.22}$$

The first two terms, as before, contain only operators that act on the spatial degrees of freedom, so

$$\hat{H}|1, 0, 0; \frac{1}{2}, m_s\rangle = (E_1 + \frac{e}{m_e c}\mathbf{B}\cdot\hat{\mathbf{S}})|1, 0, 0; \frac{1}{2}, m_s\rangle. \tag{5.23}$$

Now let us consider the magnetic field directed along the z axis. Then $\mathbf{B}\cdot\hat{\mathbf{S}} = B\hat{S}_z$. Since

$$\hat{S}_z|1,0,0;\frac{1}{2},m_s\rangle = \hbar m_s|1,0,0;\frac{1}{2},m_s\rangle \tag{5.24}$$

we see that the ket $|1,0,0;\frac{1}{2},m_s\rangle$ is an eigenket of the new Hamiltonian with eigenvalue

$$E_1 + \frac{e\hbar}{m_e c}m_s B = E_1 + 2\mu_{\mathrm{B}} m_s B. \tag{5.25}$$

So for $m_s = \frac{1}{2}$ we find the eigenvalue $E_+ = E_1 + \mu_{\mathrm{B}} B$ while for $m_s = -\frac{1}{2}$ we find the eigenvalue $E_- = E_1 - \mu_{\mathrm{B}} B$, in accordance with the experimental result. Now, let's orient the magnetic field along the x axis, so $\mathbf{B}\cdot\hat{\mathbf{S}} = B\hat{S}_x$. For notational simplicity, we omit writing the triplet 1, 0, 0 since it plays no role in the following considerations. Therefore, we write $|\frac{1}{2},m_s\rangle$ but understand the ket $|1,0,0;\frac{1}{2},m_s\rangle$. It is easy to verify that the eigenkets $\hat{S}_x$ are

$$|\psi_{x,+}\rangle \equiv \frac{1}{\sqrt{2}}\left(|\frac{1}{2},\frac{1}{2}\rangle + |\frac{1}{2},-\frac{1}{2}\rangle\right), \qquad |\psi_{x,-}\rangle \equiv \frac{1}{\sqrt{2}}\left(|\frac{1}{2},\frac{1}{2}\rangle - |\frac{1}{2},-\frac{1}{2}\rangle\right). \tag{5.26}$$

Indeed, from Eq. (4.74), we obtain $\hat{S}_x = (\hat{S}_+ + \hat{S}_-)/2$, and using Eq. (4.84), we find

$$\begin{aligned} \hat{S}_x|\psi_{x,\pm}\rangle &= \frac{1}{\sqrt{2}}\hat{S}_x\left(|\frac{1}{2},\frac{1}{2}\rangle \pm |\frac{1}{2},-\frac{1}{2}\rangle\right) \\ &= \frac{1}{2\sqrt{2}}\left(\hat{S}_-|\frac{1}{2},\frac{1}{2}\rangle \pm \hat{S}_+|\frac{1}{2},-\frac{1}{2}\rangle\right) \\ &= \frac{\hbar}{2\sqrt{2}}\left(|\frac{1}{2},-\frac{1}{2}\rangle \pm |\frac{1}{2},\frac{1}{2}\rangle\right) \\ &= \pm\frac{\hbar}{2}|\psi_{x,\pm}\rangle. \end{aligned} \tag{5.27}$$

So, $|\psi_{x,+}\rangle$ is the eigenket of $\hat{S}_x$ with eigenvalue $\hbar/2$, while $|\psi_{x,-}\rangle$ is the eigenket of $\hat{S}_x$ with eigenvalue $-\hbar/2$. It follows that

$$\hat{H}|\psi_{x,\pm}\rangle = \left(E_1 + \frac{e}{m_e c}B\hat{S}_x\right)|\psi_{x,\pm}\rangle = \left(E_1 \pm \frac{e\hbar}{2m_e c}B\right)|\psi_{x,\pm}\rangle = E_\pm|\psi_{x,\pm}\rangle. \tag{5.28}$$

The only measurable energies are then E_+ and E_-, again in accordance with the experiment. Suppose we have measured E_+ and that the electron has collapsed into the state $|\psi_{x,+}\rangle$. If we suddenly change the orientation of the magnetic field from the x-axis to the z-axis, then, according to the fourth postulate, the probability of measuring energy E_+ is given by

$$P(E_+) = |\langle\frac{1}{2},\frac{1}{2}|\psi_{x,+}\rangle|^2. \tag{5.29}$$

In fact, for a magnetic field along the z-axis, the eigenket of energy E_+ is $|\frac{1}{2}, \frac{1}{2}\rangle$, as discussed below Eq. (5.25). Taking into account Eq. (5.26), one finds immediately

$$P(E_+) = 1/2 \tag{5.30}$$

once again, in accordance with the experiment. We leave it to the reader to verify that the probability of measuring energy E_- is also the same as in the experiment.

5.2 Matrix Representation of Spin Operators

As mentioned in the previous section, elementary particles are characterized by degrees of freedom associated with spin. A basis for the Hilbert space for particles with spin s could be the set of kets $|\mathbf{r}; s, m_s\rangle$ or the set of kets $|\mathbf{p}; s, m_s\rangle$. More generally, denoting $|b_k\rangle$ as the ket of a generic orthonormal basis for the spatial part, the set of kets $|b_k; s, m_s\rangle$ forms a basis for our Hilbert space. The inner product between two kets in this basis is

$$\langle b_k; s, m_s | b_{k'}; s, m'_s\rangle = \langle b_k | b_{k'}\rangle \langle s, m_s | s, m'_s\rangle = \delta_{k,k'} \delta_{m_s, m'_s} . \tag{5.31}$$

It is also useful to define a *partial* inner product between a ket from the spatial or spin part and a ket from the new Hilbert space:

$$\langle b_k | b_{k'}; s, m'_s\rangle \equiv \langle b_k | b_{k'}\rangle |s, m'_s\rangle = \delta_{k,k'} |s, m'_s\rangle \quad \Rightarrow \quad \langle b_{k'}; s, m'_s | b_k\rangle = \delta_{k,k'} \langle s, m'_s | \tag{5.32}$$

$$\langle s, m_s | b_{k'}; s, m'_s\rangle \equiv \langle s, m_s | s, m'_s\rangle |b_{k'}\rangle = \delta_{m_s, m'_s} |b_{k'}\rangle \quad \Rightarrow \quad \langle b_{k'}; s, m'_s | s, m_s\rangle = \delta_{m_s, m'_s} \langle b_{k'} | \tag{5.33}$$

So the partial scalar product does not return a complex number but a ket (or a bra) of the spatial or spin part.

The *spatial* operators such as $\hat{\mathbf{r}}$ or $\hat{\mathbf{p}}$ or $\hat{\mathbf{L}}$, or even more exotic ones like $\hat{\mathbf{r}}$, $\hat{\mathbf{p}}^3 \hat{\mathbf{L}}^2$, act only on b_k (with m_s being mere spectators). On the other hand, the *spin* operators such as $\hat{S}_i$ or $\hat{S}^2$, or even more exotic ones like $\hat{S}_x^2 \hat{S}_z^3$, act only on m_s (with b_k being mere spectators). Therefore, the action of a generic *spatial* operator $\hat{O}^{(\text{space})}$ is given by

$$\hat{O}^{(\text{space})} |b_k; s, m_s\rangle = \sum_{k'} O^{(\text{space})}_{k'k} |b_{k'}; s, m_s\rangle \tag{5.34}$$

with

$$O^{(\text{space})}_{k'k} = \langle b_{k'}; s, m_s | \hat{O}^{(\text{space})} | b_k; s, m_s\rangle = \langle b_{k'} | \hat{O}^{(\text{space})} | b_k\rangle, \tag{5.35}$$

while the action of a generic spin operator $\hat{O}^{(\mathrm{spin})}$ is given by

$$\hat{O}^{(\mathrm{spin})}|b_k; s, m_s\rangle = \sum_{m'_s} O^{(\mathrm{spin})}_{m'_s m_s}|b_k; s, m'_s\rangle \tag{5.36}$$

with

$$O^{(\mathrm{spin})}_{m'_s m_s} = \langle b_k; s, m'_s|\hat{O}|b_k; s, m_s\rangle = \langle s, m'_s|\hat{O}|s, m_s\rangle. \tag{5.37}$$

Since spatial operators and spin operators act on different degrees of freedom, they commute with each other

$$\left[\hat{O}^{(\mathrm{space})}, \hat{O}^{(\mathrm{spin})}\right] = 0. \tag{5.38}$$

We can easily verify this fact by taking the bracket between a generic bra $\langle b_{k'}; s, m's|$ and a generic ket $|b_k; s, m_s\rangle$:

$$\begin{aligned}\langle b_{k'}; s, m'_s|\left[\hat{O}^{(\mathrm{space})}, \hat{O}^{(\mathrm{spin})}\right]|b_k; s, m_s\rangle = \sum_{k'' m''_s}\left(O^{(\mathrm{space})}_{k''k} O^{(\mathrm{spin})}_{m''_s m_s} - O^{(\mathrm{spin})}_{m''_s m_s} O^{(\mathrm{space})}_{k''k}\right)\\ \times\langle b_{k'}; s, m'_s|b_{k''}; s, m''_s\rangle.\end{aligned} \tag{5.39}$$

Since the matrix elements are simple complex numbers, the quantity in parentheses is zero.

From Eq. (5.36), we see that to determine the action of a spin operator, we can ignore the spatial part of the ket since the matrix element $O^{(\mathrm{spin})}_{m'_s m_s}$ *is the same for all* b_k. In the following, for notational convenience, we simply write $|s, m_s\rangle$, but we mean $|b_k; s, m_s\rangle$ with b_k fixed and m_s varying between $-s$ and s. Our goal is to determine the *matrix representation of spin operators* in the $|s, m_s\rangle$ basis, see Sect. 2.1. Since this is an orthonormal basis, from Eq. (4.72), it is immediately verified that the matrices $\mathbb{S}^2$ and $\mathbb{S}_z$ are diagonal

$$S^2_{m'_s, m_s} = \delta_{m'_s, m_s}\hbar^2 s(s+1), \qquad S_{z, m'_s, m_s} = \delta_{m'_s, m_s}\hbar m_s \tag{5.40}$$

In particular, the matrix $\mathbb{S}^2$ is proportional to the identity matrix with a proportionality coefficient of $\hbar^2 s(s+1)$. To obtain the representation $\mathbb{S}_x$ and $\mathbb{S}_y$ of the operators $\hat{S}_x$ and $\hat{S}_y$, we begin by observing that from Eq. (4.74), it follows that

$$\hat{S}_x = \frac{1}{2}(\hat{S}_+ + \hat{S}_-), \qquad \hat{S}_y = \frac{1}{2\mathrm{i}}(\hat{S}_+ - \hat{S}_-). \tag{5.41}$$

Hence

$$\mathbb{S}_x = \frac{1}{2}(\mathbb{S}_+ + \mathbb{S}_-), \qquad \mathbb{S}_y = \frac{1}{2\mathrm{i}}(\mathbb{S}_+ - \mathbb{S}_-). \tag{5.42}$$

Using Eq. (4.84) we find

$$S_{+,m_s',m_s} = \delta_{m_s',m_s+1}\hbar\sqrt{s(s+1)-m_s(m_s+1)}, \tag{5.43}$$

$$S_{-,m_s',m_s} = \delta_{m_s',m_s-1}\hbar\sqrt{s(s+1)-m_s(m_s-1)}. \tag{5.44}$$

Hence

$$S_{x,m_s',m_s} = \frac{\hbar}{2}\left(\delta_{m_s',m_s+1}\sqrt{s(s+1)-m_s(m_s+1)} + \delta_{m_s',m_s-1}\sqrt{s(s+1)-m_s(m_s-1)}\right), \tag{5.45}$$

$$S_{y,m_s',m_s} = \frac{\hbar}{2\mathrm{i}}\left(\delta_{m_s',m_s+1}\sqrt{s(s+1)-m_s(m_s+1)} - \delta_{m_s',m_s-1}\sqrt{s(s+1)-m_s(m_s-1)}\right). \tag{5.46}$$

The matrices $\mathbb{S}_x$ and $\mathbb{S}_y$ in the $|s, m_s\rangle$ basis have non-zero elements only above and below the diagonal. Let us have a look at a couple of examples.

5.2.1 Spin 1/2 *and Spin* 1

In the case of spin $s = 1/2$, Eq. (5.40) yields

$$\mathbb{S}^2 = \frac{3\hbar^2}{4}\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} \qquad \mathbb{S}_z = \frac{\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} \tag{5.47}$$

whereas Eqs. (5.45) and (5.46) yield

$$\mathbb{S}_x = \frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} \qquad \mathbb{S}_y = \frac{\hbar}{2}\begin{pmatrix}0 & -\mathrm{i}\\ \mathrm{i} & 0\end{pmatrix} \tag{5.48}$$

So, the spin matrices for $s = 1/2$ are proportional to the Pauli matrices introduced in Sect. 2.2:

$$\mathbb{S}_i = \frac{\hbar}{2}\sigma_i \; . \tag{5.49}$$

We can recycle some results. In particular, since the eigenvalues of $\mathbf{n}\cdot\boldsymbol{\sigma} = n_x\sigma_x + n_y\sigma_y + n_z\sigma_z$ are ± 1, then the eigenvalues of $n_x\mathbb{S}_x + n_y\mathbb{S}_y + n_z\mathbb{S}_z = \frac{\hbar}{2}(\mathbf{n}\cdot\boldsymbol{\sigma})$ are $\pm\hbar/2$ with eigenvectors given by Eq. (2.26). Setting $\varphi = 0$ and $\theta = \pi/2$, we find, see Eq. (2.22), $n_x = 1$ and $n_y = n_z = 0$. Therefore, the eigenvectors of $\mathbb{S}_x$ are

$$\psi_{x,+} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ 1\end{pmatrix}, \qquad \psi_{x,-} = \frac{1}{\sqrt{2}}\begin{pmatrix}-1\\ 1\end{pmatrix}. \tag{5.50}$$

With $\varphi = \pi/2$ and $\theta = \pi/2$, we find, see Eq. (2.22), $n_y = 1$ and $n_x = n_z = 0$. Therefore, the eigenvectors of $\mathbb{S}_y$ are

$$\boldsymbol{\psi}_{y,+} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ \mathrm{i} \end{pmatrix}, \qquad \boldsymbol{\psi}_{y,-} = \frac{1}{\sqrt{2}}\begin{pmatrix} -1 \\ \mathrm{i} \end{pmatrix}. \tag{5.51}$$

Finally, with $\theta = 0$, we find, see Eq. (2.22), $n_z = 1$ and $n_x = n_y = 0$. Therefore, the eigenvectors of $\mathbb{S}_z$ are

$$\boldsymbol{\psi}_{z,+} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad \boldsymbol{\psi}_{z,-} = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{5.52}$$

The reader can easily verify that

$$\mathbb{S}_i \boldsymbol{\psi}_{i,\pm} = \pm\frac{\hbar}{2}\boldsymbol{\psi}_{i,\pm}, \qquad i = x, y, z. \tag{5.53}$$

From the knowledge of the eigenvectors, we can then write the eigenkets of the spin operators $\hat{S}_i$ using Eq. (2.2):

$$|\psi_{i,\pm}\rangle = \sum_{m_s} \psi_{i,\pm,m_s} |\frac{1}{2}, m_s\rangle, \tag{5.54}$$

where $\psi_{i,\pm,m_s}$ is the m_s component of the vector $\boldsymbol{\psi}_{i,\pm}$. The reader can easily verify that $|\psi_{z,\pm}\rangle = |\frac{1}{2}, \pm\frac{1}{2}\rangle$, as it should be, and that $|\psi_{x,\pm}\rangle$ coincides with Eq. (5.26).

Now we consider the case of spin $s = 1$. Equation (5.40) provides

$$\mathbb{S}^2 = 2\hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbb{S}_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \tag{5.55}$$

whereas Eqs. (5.45) and (5.46) yield

$$\mathbb{S}_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \qquad \mathbb{S}_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -\mathrm{i} & 0 \\ \mathrm{i} & 0 & -\mathrm{i} \\ 0 & \mathrm{i} & 0 \end{pmatrix} \tag{5.56}$$

We leave it to the reader to verify that the matrices $\mathbb{S}_x$, $\mathbb{S}_y$, and $\mathbb{S}_z$ all have the same eigenvalues $1, 0, -1$ but, of course, different eigenvectors.

5.3 Spin-Orbit Interaction

Now that we understand that the electron is a particle with spin $s = 1/2$, let us return once again to the hydrogen atom. Suppose the electron is at an average distance r from the proton with angular momentum directed along the z-axis. In the electron's reference frame, we would see the proton orbiting around the electron at an average distance r with angular momentum directed along the z-axis. Since the proton is a particle with charge e, it generates a current and therefore a magnetic field that, according to what we have seen in Eq. (5.18), couples to the electron's spin. Therefore, the Hamiltonian $\hat{H}_0$ in Eq. (5.3) is incomplete because it does not take into account the fact that, even in the absence of external magnetic fields, there is still the magnetic field generated by the proton. To correct this deficiency, we need to evaluate the protonic magnetic field. It coincides with the field found at the center of a loop of radius r lying in the xy plane with a current flowing through it: $I = ev/(2\pi r)$, see Eq. (5.14) and Fig. 5.2. From the **law of Laplace**,[2]

$$\mathbf{B}(\mathbf{r}) = \frac{I}{c} \int \frac{d\mathbf{l} \times \mathbf{r}}{r^3}, \tag{5.57}$$

with $d\mathbf{l}$ being the infinitesimal displacement vector running along the loop in the direction of the current. Since the loop is in the xy plane, the magnetic field at its center has only a z component, and this component is given by

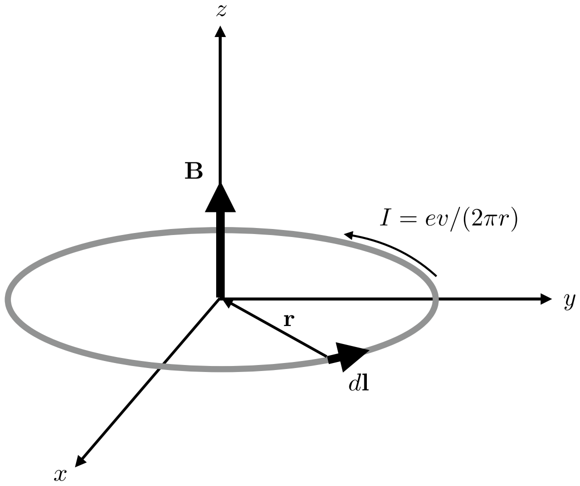

Fig. 5.2 In the electron's reference frame, the proton follows a circular trajectory of radius r, generating a magnetic field **B** that is directed along the z-axis at the origin

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[2] The law of Laplace represents the solution to the well-known Ampere's law $\nabla \times \mathbf{B} = \frac{4\pi}{c}\mathbf{J}$ in the case where $\mathbf{J}$ is the current density flowing in an extremely thin wire with cross-sectional area S, such that the current in the wire is $I = |\mathbf{J}|S$.

$$B = \frac{2\pi}{c}\frac{I}{r} = \frac{e}{c}\frac{v}{r^2} = \frac{e}{m_e c}\frac{m_e r v}{r^3} = \frac{e}{m_e c}\frac{L_z}{r^3}, \tag{5.58}$$

where L_z is the angular momentum of the electron.

The z direction in Eq. (5.58) has nothing special, so we could write this equation directly in vector form by replacing B with $\mathbf{B}$ and L_z with the angular momentum vector, which, in quantum mechanics, is the operator $\hat{\mathbf{L}}$. Substituting the resulting magnetic field $\mathbf{B}$ into Eq. (5.18), we find the following correction to the Hamiltonian of the hydrogen atom

$$\frac{e^2}{m_e^2 c^2}\frac{\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}}{\hat{r}^3}, \tag{5.59}$$

where we take into account that even r becomes an operator. The heuristic derivation of Eq. (5.59) does not consider the fact that the reference frame of the electron is not an inertial reference frame. It is not the purpose of the course to rigorously derive the form of the interaction between the electron's spin and its angular momentum. It is sufficient to say here that the result of the correct derivation differs from ours only by a factor of $1/2$. The correct operator to add to the Hamiltonian $\hat{H}_0$ of Eq. (5.3) is therefore

$$\hat{H}_{\mathrm{SO}} \equiv \frac{e^2}{2m_e^2 c^2}\frac{\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}}{\hat{r}^3} \tag{5.60}$$

and is called **spin-orbit interaction**. The spin-orbit interaction involves the dot product between the spatial operator $\hat{\mathbf{L}}$ and the spin operator $\hat{\mathbf{S}}$.

How to determine the eigenstates of the new Hamiltonian $\hat{H}_0 + \hat{H}_{\mathrm{SO}}$? The problem could easily reduce to a radial part problem only if the kets $|R, l, m; \frac{1}{2}, m_s\rangle$ were eigenstates of $\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}$, that is, if

$$\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}|R, l, m; \frac{1}{2}, m_s\rangle = \lambda_{l,m,m_s}|R, l, m; \frac{1}{2}, m_s\rangle, \tag{5.61}$$

where we denote by λ_{l,m,m_s} the eigenvalue of $\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}$ associated with the eigenstate $|R, l, m; \frac{1}{2}, m_s\rangle$. Note that the eigenvalue λ_{l,m,m_s} cannot depend on the form of the radial part since the operator $\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}$ does not contain any dependence on $\hat{r}$. If Eq. (5.61) were valid, we could always find a radial part for which the eigenvalue equation

$$(\hat{H}_0 + \hat{H}_{\mathrm{SO}})|R, l, m; \frac{1}{2}, m_s\rangle = E|R, l, m; \frac{1}{2}, m_s\rangle \tag{5.62}$$

is satisfied. From Eq. (5.61) we would have

$$(\hat{H}_0 + \hat{H}_{\text{SO}})|R, l, m; \frac{1}{2}, m_s\rangle = \left(\hat{H}_0 + \frac{e^2}{2m_e^2c^2}\frac{\lambda_{l,m,m_s}}{\hat{r}^3}\right)|R, l, m; \frac{1}{2}, m_s\rangle$$
$$= E|R, l, m; \frac{1}{2}, m_s\rangle. \tag{5.63}$$

The operator in parentheses contains only spatial operators. This means that if we were to take the *partial* scalar product with the bra $\langle\mathbf{r}|$, we would obtain

$$\langle\mathbf{r}|\left(\hat{H}_0 + \frac{e^2}{2m_e^2c^2}\frac{\lambda_{l,m,m_s}}{\hat{r}^3}\right)|R, l, m\rangle|\frac{1}{2}, m_s\rangle = E\langle\mathbf{r}|R, l, m\rangle|\frac{1}{2}, m_s\rangle. \tag{5.64}$$

Since the spin part ket is the same on both the right and left sides of the equation, this equation would be satisfied if and only if

$$\langle\mathbf{r}|\left(\hat{H}_0 + \frac{e^2}{2m_e^2c^2}\frac{\lambda_{l,m,m_s}}{\hat{r}^3}\right)|R, l, m\rangle = E\langle\mathbf{r}|R, l, m\rangle. \tag{5.65}$$

Now, let us recall that the angular part of the scalar product between the bra $\langle\mathbf{r}|$ and any ket that is an eigenket of $\hat{L}^2$ and $\hat{L}_z$, such as the ket $|R, l, m\rangle$, is the spherical harmonic $Y_{l,m}(\theta, \phi)$. In other words, $\langle\mathbf{r}|R, l, m\rangle = R(r)Y_{l,m}(\theta, \phi)$, as seen in Eq. (4.152). Taking into account that $\langle\mathbf{r}|(1/\hat{r}^3) = \langle\mathbf{r}|(1/r^3)$, we find

$$\left(-\frac{\hbar^2}{2m_e}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{\hbar^2 l(l+1)}{2m_e r^2} - \frac{e^2}{r} + \frac{e^2}{2m_e^2c^2}\frac{\lambda_{l,m,m_s}}{r^3}\right)R(r)Y_{l,m}(\theta, \phi) = ER(r)Y_{l,m}(\theta, \phi). \tag{5.66}$$

Simplifying the spherical harmonic $Y_{l,m}(\theta, \phi)$, we obtain an eigenvalue equation for the radial part only, just like in the case analyzed in Sect. 4.9. Solving this equation would then be possible to obtain the eigenvalues E in Eq. (5.63).

Unfortunately, this entire story is to be discarded. Indeed, Eq. (5.61) is incorrect. Convincing ourselves of this is quite straightforward. Let us express the dot product $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ in the following way:

$$\begin{aligned}\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} &= \hat{L}_x\hat{S}_x + \hat{L}_y\hat{S}_y + \hat{L}_z\hat{S}_z \\ &= \frac{1}{4}(\hat{L}_+ + \hat{L}_-)(\hat{S}_+ + \hat{S}_-) - \frac{1}{4}(\hat{L}_+ - \hat{L}_-)(\hat{S}_+ - \hat{S}_-) + \hat{L}_z\hat{S}_z \\ &= \frac{1}{2}(\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+) + \hat{L}_z\hat{S}_z.\end{aligned} \tag{5.67}$$

Acting on the ket $|n, l, m; \frac{1}{2}, m_s\rangle$ with $\hat{L}_+\hat{S}_-$ results in a ket with m increased by one and m_s decreased by one. Conversely, acting with $\hat{L}_-\hat{S}_+$ results in a ket with m decreased by one and m_s increased by one. The kets $|n, l, m; \frac{1}{2}, m_s\rangle$ are only eigenkets of $\hat{L}_z\hat{S}_z$ with eigenvalue $\hbar^2 m m_s$ but not eigenkets of the dot product $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$. So, who are the eigenkets of $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$?

5.4 Addition of Angular Momenta

In this section, we address the question posed at the end of the previous section. To simplify notation, we omit writing the radial index n since it is a mere spectator, meaning it never changes under the action of angular momentum and spin operators. We write $|l, m; s, m_s\rangle$ but understand it as $|n, l, m; s, m_s\rangle$. Additionally, we solve the problem for a general s since the form of the spin-orbit interaction often appears in physics and is not limited to particles with $s = 1/2$.

We begin by recalling that the ket $|l, m; s, m_s\rangle$ is the state in which the electron collapses when a measurement of $\hat{L}^2$ yields the value $\hbar^2 l(l+1)$, a measurement of $\hat{L}_z$ yields the value $\hbar m$, a measurement of $\hat{S}^2$ yields the value $\hbar^2 s(s+1)$, and a measurement of $\hat{S}_z$ yields the value $\hbar m_s$. The operators $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, and $\hat{S}_z$ all commute with each other, and the set of kets $|l, m; s, m_s\rangle$ forms their common basis of eigenvectors, as discussed in point (6) of Sect. 1.9. Now, let us consider the **total angular momentum** operator:

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}, \tag{5.68}$$

whose square is (remember that a spatial operator always commutes with a spin operator)

$$\hat{J}^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \tag{5.69}$$

It is straightforward to show that the components of $\hat{\mathbf{J}}$ satisfy the same commutation rules as the angular momentum:

$$[\hat{J}_i, \hat{J}_j] = [\hat{L}_i, \hat{L}_j] + [\hat{S}_i, \hat{S}_j] = \mathrm{i}\hbar \sum_k \varepsilon_{ijk}(\hat{L}_k + \hat{S}_k) = \mathrm{i}\hbar \sum_k \varepsilon_{ijk} \hat{J}_k. \tag{5.70}$$

Therefore, $\hat{J}^2$ has eigenvalues $\hbar^2 j(j+1)$ and $\hat{J}_z$ has eigenvalues $\hbar m_j$ with $m_j = -j, \ldots, j$. Moreover, both $\hat{L}^2$ and $\hat{S}^2$ commute, not only with each other but also with $\hat{J}_z$ and $\hat{J}^2$. We leave this simple verification to the reader. Thus, in addition to the basis $|l, m; s, ms\rangle$, we could consider the basis consisting of the common eigenkets of the operators $\hat{J}^2$, $\hat{J}_z$, $\hat{L}^2$, and $\hat{S}^2$. Let $|j, m_j\rangle_{ls}$ denote the kets of this basis. We then have:

$$\begin{aligned}
\hat{J}^2 |j, m_j\rangle_{ls} &= \hbar^2 j(j+1) |j, m_j\rangle_{ls} \\
\hat{J}_z |j, m_j\rangle_{ls} &= \hbar m_j |j, m_j\rangle_{ls} \\
\hat{L}^2 |j, m_j\rangle_{ls} &= \hbar^2 l(l+1) |j, m_j\rangle_{ls} \\
\hat{S}^2 |j, m_j\rangle_{ls} &= \hbar^2 s(s+1) |j, m_j\rangle_{ls}
\end{aligned} \tag{5.71}$$

The advantage of working with this new basis is that the kets $|j, m_j\rangle_{ls}$ are precisely the eigenkets of $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$. In fact, from Eq. (5.69), we have

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{1}{2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2), \tag{5.72}$$

and hence

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}|j, m_j\rangle_{ls} = \frac{\hbar^2}{2}\left(j(j+1) - l(l+1) - s(s+1)\right)|j, m_j\rangle_{ls}. \tag{5.73}$$

The new kets $|j, m_j\rangle_{ls}$ must be expressible as linear combinations of the old kets $|l, m; s, m_s\rangle$ (forming the latter a basis). In the remainder of this section, we find the possible values of j and how to express the new kets in terms of the old ones. We then learn about the **addition of angular momenta**. Let us start by noting that all kets in the old basis are eigenkets of $\hat{L}^2$ with the same eigenvalue $\hbar^2 l(l+1)$ and of $\hat{S}^2$ with the same eigenvalue $\hbar^2 s(s+1)$. Therefore, any linear combination of them automatically satisfies the last two relations in Eq. (5.71). Furthermore, the old kets are also eigenkets of $\hat{J}_z$ since

$$\hat{J}_z|l, m; s, m_s\rangle = (\hat{L}_z + \hat{S}_z)|l, m; s, m_s\rangle = \hbar(m + m_s)|l, m; s, m_s\rangle. \tag{5.74}$$

It follows that *the kets of the new basis must be linear combinations of the kets of the old basis with the same value of the sum* $m + m_s$. Indeed, if we were to mix kets from the old basis with different values of $m + m_s$, we could not generate an eigenket of $\hat{J}_z$. Having denoted $\hbar m_j$ as the eigenvalues of $\hat{J}_z$, we can then write:

$$|j, m_j\rangle_{ls} = \sum_{m, m_s : m + m_s = m_j} C^{(j)}_{m, m_s}|l, m; s, m_s\rangle. \tag{5.75}$$

The reader can easily convince themselves that regardless of the coefficients $C^{(j)}_{m,ms}$, this is an eigenket of $\hat{J}_z$ with eigenvalue $\hbar m_j$ (and obviously also of $\hat{L}^2$ and $\hat{S}^2$ with eigenvalues $\hbar^2 l(l+1)$ and $\hbar^2 s(s+1)$ respectively). It is necessary, therefore, to determine the coefficients $C^{(j)}_{m,ms}$ so that the ket in Eq. (5.75) is also an eigenket of $\hat{J}^2$. To this end, we observe that the maximum possible value of m_j is the sum of the maximum possible values of m and m_s, i.e., $m = l$ and $m_s = s$. Since there is only one ket in the old basis for which $m + m_s = l + s$, the linear combination in Eq. (5.75) consists of the sole ket $|l, l; s, s\rangle$. This must also be a ket in the new basis with $m_j = l + s$. But to which value of j does it correspond? Since m_j can vary between $-j$ and j, and it is not possible to construct kets with m_j greater than $l + s$, we deduce that $j = l + s$. This is also the maximum value that j can assume, as if it were not the case, it would be possible to construct states with $m_j > l + s$, which is absurd. Thus, we have established that

$$|l + s, l + s\rangle_{ls} = |l, l; s, s\rangle. \tag{5.76}$$

We can immediately generate a second eigenket of the new basis by applying the operator

$$\hat{J}_- = \hat{L}_- + \hat{S}_-. \tag{5.77}$$

Indeed, using Eq. (4.84), we have

$$\begin{aligned}
\hat{J}_-|\underbrace{l+s}_{j},\underbrace{l+s}_{m_j}\rangle_{ls} &= \hbar\sqrt{\underbrace{(l+s)}_{j}\underbrace{(l+s+1)}_{j+1}-\underbrace{(l+s)}_{m_j}\underbrace{(l+s-1)}_{m_j-1}}\,|\underbrace{l+s}_{j},\underbrace{l+s-1}_{m_j-1}\rangle_{ls}\\
&= (\hat{L}_- + \hat{S}_-)|l,l;s,s\rangle\\
&= \hbar\sqrt{l(l+1)-l(l-1)}\,|l,l-1;s,s\rangle\\
&+ \hbar\sqrt{s(s+1)-s(s-1)}\,|l,l;s,s-1\rangle
\end{aligned} \tag{5.78}$$

from which it follows that

$$\begin{aligned}
|l+s,l+s-1\rangle_{ls} &= \frac{\sqrt{l(l+1)-l(l-1)}}{\sqrt{(l+s)(l+s+1)-(l+s)(l+s-1)}}|l,l-1;s,s\rangle\\
&+ \frac{\sqrt{s(s+1)-s(s-1)}}{\sqrt{(l+s)(l+s+1)-(l+s)(l+s-1)}}|l,l;s,s-1\rangle.
\end{aligned} \tag{5.79}$$

Correctly, the ket $|l+s,l+s-1\rangle_{ls}$ in Eq. (5.79), which by construction is an eigenket of $\hat{J}_z$ with eigenvalue $\hbar(l+s-1)$, is a linear combination of the only two kets in the old basis for which $m+m_s = l+s-1$, see Eq. (5.75). By applying the operator $\hat{J}_-$ on the left and $\hat{L}_- + \hat{S}_-$ on the right in Eq. (5.79), we obtain the ket $|l+s,l+s-2\rangle_{ls}$ of the new basis written in terms of kets from the old basis. Continuing to apply the operator $\hat{J}_-$ on the left and $\hat{L}_- + \hat{S}_-$ on the right generates kets of the new basis with decreasing values of m_j, that is, with $m_j = l+s-3, l+s-4$, etc., until reaching $m_j = -l-s$. At this point, as we know from the theory in Sect. 4.6, the application of $\hat{J}_-$ to the ket $|l+s,-l-s\rangle_{ls}$ produces the null ket, and thus the algorithm terminates.

We have thus found a total of $2(l+s)+1$ kets of the new basis with $j=l+s$ and $m_j = -l-s,\ldots,l+s$. We say that all these kets belong to the "chain" with $j=l+s$, see Fig. 5.3. Obviously, there must be other kets in the new basis since the total number of kets in the old basis is $(2l+1)(2s+1) > 2(l+s)+1$. To find them, let us make the following consideration. Using the only two kets of the old basis with $m+m_s = l+s-1$, we can only make an orthonormal linear combination to that in Eq. (5.79). It is obtained by exchanging the coefficients and changing the sign of one of the two coefficients. Indeed, if $|\Psi_1\rangle$ and $|\Psi_2\rangle$ are two orthonormal kets, which are the two kets of the linear combination in Eq. (5.79), and if we consider the linear combination $\alpha|\Psi_1\rangle + \beta|\Psi_2\rangle$ with $|\alpha|^2+|\beta|^2=1$, then the linear combination $\beta|\Psi_1\rangle - \alpha|\Psi_2\rangle$ is orthogonal to the first one and normalized to one. The orthonormal linear combination to that of Eq. (5.79) must necessarily be a ket of the new basis because:

(1) The kets of the new basis are orthonormal to each other, and
(2) The kets of the new basis must have the fixed sum $m + m_s$.

In general, these two conditions are necessary but not sufficient to ensure that a ket belongs to the new basis. However, in the case we are examining, they are also sufficient because there is only one linear combination of the kets of the old basis that is orthogonal to that of Eq. (5.79) and at the same time has $m_j = m + m_s = l + s - 1$.

To which value of j does this new ket correspond? As we have said, j can at most be $l + s$, and since $m_j = l + s - 1$, it could be either $j = l + s$ or $j = l + s - 1$ (remember once again that m_j cannot be greater than j). If j were equal to $l + s$, it would be possible to generate, by applying $\hat{J}_+ = \hat{L}_+ + \hat{S}_+$, a second ket beyond the one in Eq. (5.76), with $j = l + s$ and $m_j = l + s$. However, this is absurd since there is only one ket with such quantum numbers. We conclude that $j = l + s - 1$. Inverting the coefficients of the linear combination in Eq. (5.79) and changing the sign of one of them, we can then write that

$$\begin{aligned} |l+s-1, l+s-1\rangle_{ls} = {} & \frac{\sqrt{s(s+1) - s(s-1)}}{\sqrt{(l+s)(l+s+1) - (l+s)(l+s-1)}} |l, l-1; s, s\rangle \\ & - \frac{\sqrt{l(l+1) - l(l-1)}}{\sqrt{(l+s)(l+s+1) - (l+s)(l+s-1)}} |l, l; s, s-1\rangle, \end{aligned} \tag{5.80}$$

We can now proceed as before to recursively determine all the kets in the chain with $j = l + s - 1$, see Fig. 5.3. It is sufficient to apply the operator $\hat{J}_-$ on the left and $\hat{L}_- + \hat{S}_-$ on the right to obtain all the kets $|l + s - 1, m_j\rangle_{ls}$ with $m_j = l + s - 2, l + s - 3, \ldots, -l - s + 1$, for a total of $2(l + s - 1) + 1$ kets.

Now let us consider the kets $|l + s, l + s - 2\rangle_{ls}$ (the third ket in the chain with $j = l + s$) and $|l + s - 1, l + s - 2\rangle_{ls}$ (the second ket in the chain with $j = l + s - 1$), see Fig. 5.3. They have the same $m_j = l + s - 2$, and therefore, they are linear combinations of the old kets with $m + m_s = l + s - 2$. Of these old kets, there can be at most three, as we can have $m = l$ and $m_s = s - 2$ or $m = l - 1$ and $m_s = s - 1$ or $m = l - 2$ and $m_s = s$. Therefore, the two new kets $|l + s, l + s - 2\rangle_{ls}$ and $|l + s - 1, l + s - 2\rangle_{ls}$ are linear combinations of these three old kets. With these three old kets, we can then construct a single orthonormal linear combination of the new kets $|l + s, l + s - 2\rangle_{ls}$ and $|l + s - 1, l + s - 2\rangle_{ls}$. For the same reasons as before, this linear combination must be a ket of the new basis, and since there cannot be more than two kets with $m_j = l + s - 1$, it must belong to the chain with $j = l + s - 2$. Thus, we obtain the ket $|l + s - 2, l + s - 2\rangle_{ls}$ from which we can generate all the kets in the chain with $j = l + s - 2$ by applying the operator $\hat{J}_-$ on the right and $\hat{L}_- + \hat{S}_-$ on the left.

Continuing with the algorithm just described, it is possible to construct the ket $|l + s - 3, l + s - 3\rangle_{ls}$, from which all the kets in the chain with $j = l + s - 3$ can be generated. Then, the ket $|l + s - 4, l + s - 4\rangle_{ls}$ can be constructed, from which all the kets in the chain with $j = l + s - 4$ can be generated, and so on. When does this procedure end? Finding the answer is rather straightforward. The chain with a certain j contains $2j + 1$ kets, and the possible values of j are, as we have seen,

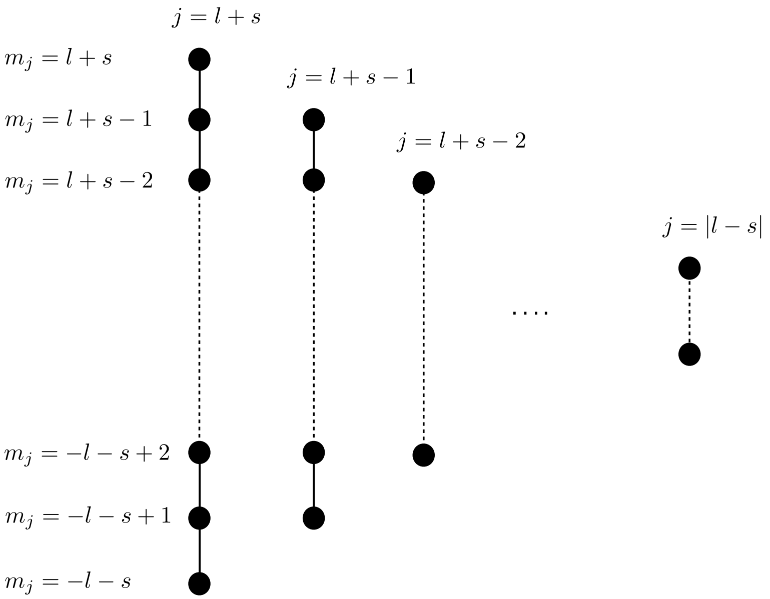

Fig. 5.3 Struttura degli autokets del momento angolare totale. Essi formano delle “catene” caratterizzate da valori diversi di j. I valori di j vanno da un massimo di $l + s$ a un minimo di $|l - s|$

$l + s, l + s - 1, l + s - 2$, etc. Since the number of kets in the old basis and the new basis is the same, there must necessarily exist a minimum value of j, let us call it $j_{\min}$, that guarantees this. Remembering that the number of kets in the old basis is $(2l + 1)(2s + 1)$ and that a chain with a given j consists of $(2j + 1)$ kets, the value of $j_{\min}$ must be such that

$$\sum_{j=j_{\min}}^{l+s} (2j + 1) = (2l + 1)(2s + 1). \tag{5.81}$$

We have

$$\begin{aligned}\sum_{j=j_{\min}}^{l+s} (2j + 1) &= 2\left(\sum_{j=1}^{l+s} j - \sum_{j=1}^{j_{\min}-1} j\right) + l + s - j_{\min} + 1\\ &= (l + s + 1)(l + s) - j_{\min}(j_{\min} - 1) + l + s - j_{\min} + 1\\ &= (l + s + 1)^2 - j_{\min}^2 \,.\end{aligned} \tag{5.82}$$

Inserting this result into Eq. (5.81) and isolating $j_{\min}$

$$\begin{aligned} j_{\min}^2 &= (l+s+1)^2 - (2l+1)(2s+1) \\ &= (l+s)^2 + 2(l+s) + 1 - 4ls - 2(l+s) - 1 \\ &= (l-s)^2 \end{aligned} \tag{5.83}$$

and since $j_{\min} \geq 0$, we conclude that

$$j_{\min} = |l - s|. \tag{5.84}$$

In Fig. 5.3, we show the structure of the new basis.

The result regarding the possible values of j is quite intuitive to remember. The total angular momentum is the sum of two vectors. Classically, if we denote $\hbar l$ and $\hbar s$ as the lengths of these two vectors, then the maximum possible length of their sum is achieved when the two vectors are parallel, and it is $\hbar(l+s)$, while the minimum possible length of the sum is achieved when the two vectors are antiparallel, and it is $\hbar|l-s|$.

Finally, it is worth noting that the theory of addition of angular momenta is entirely general and not limited to cases involving the angular momentum operators $\hat{\mathbf{L}}$ and spin $\hat{\mathbf{S}}$. For example, in systems with two particles, there might be a convenience in working in the basis of the total angular momentum $\hat{\mathbf{L}}_{\text{tot}} = \hat{\mathbf{L}}_1 + \hat{\mathbf{L}}_2$. All the previous results still apply; one just needs to identify $\hat{\mathbf{J}}$ with $\hat{\mathbf{L}}_{\text{tot}}$, $\hat{\mathbf{L}}$ with $\hat{\mathbf{L}}_1$, and $\hat{\mathbf{S}}$ with $\hat{\mathbf{L}}_2$.

5.4.1 Hydrogen Atom with Spin-Orbit Interaction

We can use what we have just learned to calculate eigenvalues and eigenfunctions of the Hamiltonian of the hydrogen atom with spin-orbit interaction. It is possible to reduce the general problem to an eigenvalue equation for the radial part only. If we reintroduce the principal quantum number into the eigenkets $|j, m_j\rangle_{ls}$, we have, according to Eq. (5.73),

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} |n, j, m_j\rangle_{ls} = \frac{\hbar^2}{2} \left(j(j+1) - l(l+1) - s(s+1) \right) |n, j, m_j\rangle_{ls} \, . \tag{5.85}$$

Therefore, given a linear combination of eigenkets of the *total angular momentum* that mixes only kets with different principal quantum numbers

$$|R, j, m_j\rangle_{ls} = \sum_n R_n |n, j, m_j\rangle_{ls}, \tag{5.86}$$

we have

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} |R, j, m_j\rangle_{ls} = \frac{\hbar^2}{2} \left(j(j+1) - l(l+1) - s(s+1) \right) |R, j, m_j\rangle_{ls}. \tag{5.87}$$

Let us show that it is possible to choose the kets $|R, j, m_j\rangle_{ls}$ in such a way that they satisfy the eigenvalue equation

$$(\hat{H}_0 + \hat{H}_{\mathrm{SO}})|R, j, m_j\rangle_{ls} = E|R, j, m_j\rangle_{ls}. \tag{5.88}$$

Taking into account Eq. (5.87), we have

$$\begin{aligned}(\hat{H}_0 + \hat{H}_{\mathrm{SO}})|R, j, m_j\rangle_{ls} &= \left(\hat{H}_0 + \frac{e^2}{2m_e^2c^2}\frac{\hbar^2}{2}\frac{j(j+1) - l(l+1) - s(s+1)}{\hat{r}^3}\right)|R, j, m_j\rangle_{ls}\\ &= E|R, j, m_j\rangle_{ls}.\end{aligned} \tag{5.89}$$

The operator in parentheses now contains only spatial operators. Keeping in mind that the ket $|R, j, m_j\rangle_{ls}$ is a linear combination of kets with a fixed l, if we take the partial inner product with the bra $\langle\mathbf{r}|$, we find

$$\begin{aligned}\left(-\frac{\hbar^2}{2m_e}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{\hbar^2 l(l+1)}{2m_e r^2} - \frac{e^2}{r} + \frac{e^2}{2m_e^2c^2}\frac{\hbar^2}{2}\frac{j(j+1) - l(l+1) - s(s+1)}{r^3}\right)&\\ \langle\mathbf{r}|R, j, m_j\rangle_{ls}&\\ = E\langle\mathbf{r}|R, j, m_j\rangle_{ls}&\end{aligned} \tag{5.90}$$

Note that in parentheses, only the radial coordinate r appears. Using Eq. (5.75), we see that

$$\langle\mathbf{r}|R, j, m_j\rangle_{ls} = R(r)\sum_{m,m_s : m+m_s=m_j} C^{(j)}_{m,m_s} Y_{l,m}(\theta,\phi)|s, m_s\rangle. \tag{5.91}$$

So, at fixed l and j, Eq. (5.90) is satisfied if and only if the radial part satisfies

$$\begin{aligned}\left(-\frac{\hbar^2}{2m_e}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{\hbar^2 l(l+1)}{2m_e r^2} - \frac{e^2}{r} + \frac{e^2}{2m_e^2c^2}\frac{\hbar^2}{2}\frac{j(j+1) - l(l+1) - s(s+1)}{r^3}\right)R(r)&\\ = ER(r).&\end{aligned}$$

We have therefore reduced the original problem to an eigenvalue problem for the radial part only, to be solved for every possible value of j, l, and s. In our case, $s = 1/2$ is the only possible value, as the electron is a spin-1/2 particle. So, for $l = 0$, we can only have $j = 1/2$, while for $l > 0$, we can have both $j = l - 1/2$ and $j = l + 1/2$. The radial eigenfunctions and the corresponding eigenvalues depend on a principal quantum number, let us call it Q, as well as j and l. Once the radial function $R_{Q,j,l}(r)$ with eigenvalue $E_{Q,j,l}$ is known, we can construct the eigenkets of the entire Hamiltonian $\hat{H}_0 + \hat{H}_{\mathrm{SO}}$. It is sufficient to calculate the coefficients R_n in Eq. (5.86). This means that we need to calculate

$$R_n = {}_{ls}\langle n, j, m_j | R_{Q,j,l}, j, m_j \rangle_{ls} = \int dr\, r^2 R_{n,l}(r) R_{Q,j,l}(r), \tag{5.92}$$

where $R_{n,l}$ are the radial wave functions of the hydrogen atom studied in Sect. 4.9.2.

5.4.2 Heisenberg Hamiltonian for Magnetic Systems

Crystals are physical structures characterized by a unit cell that repeats periodically in space, and within which there is a finite number of atoms positioned in the same way. Crystals can be characterized based on their electronic properties, such as conductivity, optical properties, such as their color, and magnetic properties. Regarding the latter, they emerge, for example, in crystals where the number of electrons in each cell is odd, and therefore, each cell has an effective spin different from zero. The magnetism in these materials is essentially due to the fact that the spin of one cell interacts with the spin of the neighboring cell, and the energy associated with this interaction is minimized when the spins are aligned. The Hamiltonian that governs the spins of the cells is called the **Heisenberg Hamiltonian**, and it has the following mathematical form:

$$\hat{H} = \sum_{ij} J_{ij}\, \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j \tag{5.93}$$

where $\hat{\mathbf{S}}_i$ is the spin operator of the i-th cell, and J_{ij} are coupling constants (they have nothing to do with the total angular momentum studied earlier). Let us see how the theory of addition of angular momenta helps us in understanding magnetism in materials.

Suppose, for simplicity, that we have only two cells, and denote by $\hat{\mathbf{S}}_1$ and $\hat{\mathbf{S}}_2$ the spins of these cells. Then the Hamiltonian becomes:

$$\hat{H} = J\, \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_1, \tag{5.94}$$

where we define the coupling constant $J \equiv J_{12}$. Introducing the operator of the total spin:

$$\hat{\mathbf{S}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_1 \tag{5.95}$$

we can rewrite the Hamiltonian using Eq. (5.72) as follows:

$$\hat{H} = \frac{J}{2}(\hat{S}^2 - \hat{S}_1^2 - \hat{S}_2^2). \tag{5.96}$$

If the spins of both cells are 1/2, then the possible values of the total spin are $s = 1$ or $s = 0$, and the eigenvalues of $\hat{H}$ are:

$$E_s = \frac{J\hbar^2}{2}\left(s(s+1) - \frac{3}{2}\right). \tag{5.97}$$

In the case where $J < 0$, we see that the lowest energy is achieved for $s = 1$, and the corresponding eigenkets of the Hamiltonian are

$$\begin{aligned}
|1, 1\rangle_{\frac{1}{2}\frac{1}{2}} &= |\frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle \\
|1, 0\rangle_{\frac{1}{2}\frac{1}{2}} &= \frac{1}{\sqrt{2}}\left(|\frac{1}{2}, \frac{1}{2}; \frac{1}{2}, -\frac{1}{2}\rangle + |\frac{1}{2}, -\frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle\right) \\
|1, -1\rangle_{\frac{1}{2}\frac{1}{2}} &= |\frac{1}{2}, -\frac{1}{2}; \frac{1}{2}, -\frac{1}{2}\rangle.
\end{aligned} \tag{5.98}$$

These three states are called **triplet states**. The first and the third of them have the spins of the two cells aligned with each other. On the other hand, the state with higher energy with $s = 0$, also called the **singlet state**,

$$|0, 0\rangle_{\frac{1}{2}\frac{1}{2}} = \frac{1}{\sqrt{2}}\left(|\frac{1}{2}, \frac{1}{2}; \frac{1}{2}, -\frac{1}{2}\rangle - |\frac{1}{2}, -\frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle\right) \tag{5.99}$$

has the spins of the cells anti-aligned. This simple example helps us understand how the Heisenberg interaction favors a certain alignment of spins and, therefore, magnetism.

One last observation about notation. When dealing with spin operators for $s = 1/2$, the corresponding eigenkets are often written more compactly as:

$$|+\rangle \equiv |\frac{1}{2}, \frac{1}{2}\rangle, \qquad |-\rangle \equiv |\frac{1}{2}, -\frac{1}{2}\rangle. \tag{5.100}$$

This more compact notation can also be used for simultaneous eigenkets of two spin operators for $s = 1/2$. For example:

$$\begin{aligned}
|+; +\rangle &= |\frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle, \qquad |+; -\rangle = |\frac{1}{2}, \frac{1}{2}; \frac{1}{2}, -\frac{1}{2}\rangle \\
|-; +\rangle &= |\frac{1}{2}, -\frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle, \qquad |-; -\rangle = |\frac{1}{2}, -\frac{1}{2}; \frac{1}{2}, -\frac{1}{2}\rangle
\end{aligned} \tag{5.101}$$

In the more compact notation, the triplet states in Eq. (5.98) can be written as:

$$\begin{aligned}
|1, 1\rangle_{\frac{1}{2}\frac{1}{2}} &= |+; +\rangle \\
|1, 0\rangle_{\frac{1}{2}\frac{1}{2}} &= \frac{1}{\sqrt{2}}\left(|+; -\rangle + |-; +\rangle\right) \\
|1, -1\rangle_{\frac{1}{2}\frac{1}{2}} &= |-; -\rangle.
\end{aligned} \tag{5.102}$$

while the singlet state in Eq. (5.103) is written as:

$$|0,0\rangle_{\frac{1}{2}\frac{1}{2}} = \frac{1}{\sqrt{2}}\left(|+;-\rangle - |-;+\rangle\right) \tag{5.103}$$

5.5 Exercises

1. Consider a particle of spin 1/2 on a sphere and let $|l, m_l; s, m_s\rangle$ be the simultaneous eigenstates of the operators of orbital angular momentum $\hat{L}^2$ e $\hat{L}_z$ with eigenvalues $\hbar^2 l(l+1)$ and $\hbar m_l$, and of the spin operators $\hat{S}^2$ and $\hat{S}_z$ with eigenvalues $\hbar^2 s(s+1)$ and $\hbar m_s$ (for the hypothesis $s = 1/2$). Said $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$ is the total angular momentum, a simultaneous measurement of $\hat{J}^2$, $\hat{J}_z$ and $\hat{L}^2$ provides for the first two operators the values $15\hbar^2/4$ and $\hbar/2$ with probability 1 and for the third operator the value $2\hbar^2$ with probability 1/2.
   i. Write the ket of the system in terms of the eigenkets of the total angular momentum $|j, m_j\rangle_{ls}$.
   ii. Calculate the average value at time t of the operator $\hat{L}_x\hat{S}_x + \hat{L}_y\hat{S}_y$ if the Hamiltonian of the system is $\hat{H} = \epsilon\hat{L}_z/\hbar$. (Hint: Expand the states $|j, m_j\rangle_{l,s}$ in the basis $|l, m_l; s, m_s\rangle$).

Solution *We denote by* $|j, m_j; l, \frac{1}{2}\rangle$ *the simultaneous eigenstates of* J^2, J_z, L^2, S^2 *with eigenvalues* $\hbar^2 j(j+1)$, $\hbar m_j$, $\hbar^2 l(l+1)$ *and* $3\hbar^2/4$ *respectively. From the problem data* $\hbar^2 j(j+1) = 15\hbar^2/4$, *then* $j = 3/2$, *and* $m_j = 1/2$. *For* $s = 1/2$ *the value of* j *can be obtained both with* $l = 1$ *and with* $l = 2$. *So the most generic ket* $|\Psi\rangle$ *compatible with the measures of* J^2 *and* J_z *is*

$$|\Psi\rangle = \alpha|\frac{3}{2},\frac{1}{2};1,\frac{1}{2}\rangle + \beta|\frac{3}{2},\frac{1}{2};2,\frac{1}{2}\rangle$$

with $|\alpha|^2 + |\beta|^2 = 1$. *It is convenient to express the two states as a linear combination of the kets* $|l, m_l\rangle|\frac{1}{2}, m_s\rangle$ *in order to determine the temporal evolution. We have*

$$|\frac{3}{2},\frac{1}{2};1,\frac{1}{2}\rangle = \sqrt{\frac{2}{3}}|1,0\rangle|\frac{1}{2},\frac{1}{2}\rangle + \sqrt{\frac{1}{3}}|1,1\rangle|\frac{1}{2},-\frac{1}{2}\rangle$$

$$|\frac{3}{2},\frac{1}{2};2,\frac{1}{2}\rangle = \sqrt{\frac{6}{15}}|2,0\rangle|\frac{1}{2},\frac{1}{2}\rangle - \sqrt{\frac{9}{15}}|2,1\rangle|\frac{1}{2},-\frac{1}{2}\rangle$$

So the state of the system at time t *turns out to be*

$$|\Psi(t)\rangle = \alpha\left(\sqrt{\frac{2}{3}}|1,0\rangle|\frac{1}{2},\frac{1}{2}\rangle + e^{-\mathrm{i}\epsilon t}\sqrt{\frac{1}{3}}|1,1\rangle|\frac{1}{2},-\frac{1}{2}\rangle\right) + \beta\left(\sqrt{\frac{6}{15}}|2,0\rangle|\frac{1}{2},\frac{1}{2}\rangle - e^{-\mathrm{i}\epsilon t}\sqrt{\frac{9}{15}}|2,1\rangle|\frac{1}{2},-\frac{1}{2}\rangle\right)$$

Let's now observe that

$$\langle\Psi(t)|L_xS_x + L_yS_y|\Psi(t)\rangle = \frac{1}{2}\langle\Psi(t)|L_+S_- + L_-S_+|\Psi(t)\rangle = \mathrm{Re}[\langle\Psi(t)|L_+S_-|\Psi(t)\rangle].$$

So

$$\langle\Psi(t)|L_xS_x + L_yS_y|\Psi(t)\rangle = \hbar^2\left(|\alpha|^2\frac{2}{3} - |\beta|^2\frac{18}{15}\right)\cos(\epsilon t)$$

Since the probability of measuring $l = 1$ is $1/2$ we have $|\alpha|^2 = |\beta|^2 = 1/2$ and therefore

$$\langle\Psi(t)|L_xS_x + L_yS_y|\Psi(t)\rangle = -\frac{4}{15}\hbar^2\cos(\epsilon t)$$

2. Two particles of spin 1/2 are in the following non-normalized state

$$|\psi\rangle = \sqrt{3}\mathrm{i}|\frac{1}{2},\frac{1}{2};\frac{1}{2},\frac{1}{2}\rangle - \sqrt{2}|\frac{1}{2},\frac{1}{2};\frac{1}{2},-\frac{1}{2}\rangle + \sqrt{2}\mathrm{i}|\frac{1}{2},-\frac{1}{2};\frac{1}{2},\frac{1}{2}\rangle + (1+\mathrm{i})|\frac{1}{2},-\frac{1}{2};\frac{1}{2},-\frac{1}{2}\rangle$$

i. Normalize the state
ii. Calculate the probability that a measure of the total spin $\hat{S}^2$ provides $2\hbar^2$ and 0.
iii. Are other values possible for a measure of $\hat{S}^2$?
iv. Calculate $\langle\psi|\hat{S}^2|\psi\rangle$

Solution *The norm of the state is 3. In the basis of the total spin $|S, M_S\rangle$ the normalized state is written as*

$$|\psi\rangle = \frac{1}{3}\left(\sqrt{3}\mathrm{i}|1,1\rangle - (1-\mathrm{i})|1,0\rangle - (1+\mathrm{i})|0,0\rangle + (1+\mathrm{i})|1,-1\rangle\right)$$

So the probability of measuring $2\hbar^2$ is $7/9$ while that of measuring 0 is $2/9$. Therefore the average value $\langle\psi|S^2|\psi\rangle = 14/9\hbar^2$. No other values for a measure of S^2 is possible.

3. Let a system of two particles be given, one with spin $S_1 = 1$ and one of spin $S_2 = 1/2$. This system is investigated experimentally and the following information is extracted

(1) A measure of the square of the total spin $S^2 = (\mathbf{S}_1 + \mathbf{S}_2) \cdot (\mathbf{S}_1 + \mathbf{S}_2)$ provides the value $(3/4)\hbar^2$ with probability $1/3$
(2) A measure of the total spin along the z axis, i.e $S_z = S_{1,z} + S_{2,z}$, provides the value $(3/2)\hbar$ with probability $2/3$.
(3) The average of the total spin along the z axis is equal to $(5/6)\hbar$
(4) The average of the operator $\hat{S}^2_{1,-}$ is equal to $\frac{4\hbar^2}{3\sqrt{3}}\mathrm{i}$
Determine the normalized state of the system.
Solution *We denote by* $|j, m\rangle$ *the eigenstates of the total spin. The most general state is*

$$|\psi\rangle = \sum_{m=-3/2}^{3/2} \alpha_m |\frac{3}{2}, m\rangle + \sum_{m=-1/2}^{1/2} \beta_m |\frac{1}{2}, m\rangle$$

From information (1) we obtain $\sum_{m=-1/2}^{1/2} |\beta_m|^2 = 1/3$. *We can conveniently write this constraint as* $\beta_{1/2} = \frac{1}{\sqrt{3}} e^{\mathrm{i}\phi_1} \sin\theta$ *e* $\beta_{-1/2} = \frac{1}{\sqrt{3}} e^{\mathrm{i}\phi_2} \cos\theta$ *where the angles* ϕ_1, ϕ_2 *and* θ *are yet to be determined. From information (2) we obtain* $|\alpha_{3/2}|^2 = 2/3$ *and since* $\sum_{m=-3/2}^{3/2} |\alpha_m|^2 = 1 - \frac{1}{3} = \frac{2}{3}$ *we conclude that* $\alpha_{1/2} = \alpha_{-1/2} = \alpha_{-3/2} = 0$. *So the state searched has the form* $|\psi\rangle = \sqrt{\frac{2}{3}}\, |\frac{3}{2}, \frac{3}{2}\rangle + \frac{1}{\sqrt{3}} \left(e^{\mathrm{i}\phi_1} \sin\theta |\frac{1}{2}, \frac{1}{2}\rangle + e^{\mathrm{i}\phi_2} \cos\theta |\frac{1}{2}, -\frac{1}{2}\rangle \right)$. *From information (3) we obtain* $\langle\psi|\hat{S}_z|\psi\rangle = \hbar(1 + \frac{1}{6}\sin^2\theta - \frac{1}{6}\cos^2\theta) = \frac{5}{6}\hbar$ *from which it follows* $\cos\theta = 1$ *and* $\sin\theta = 0$. *We ended up having to determine only the* ϕ_2 *phase. Taking into account the fact that* $|\frac{3}{2}, \frac{3}{2}\rangle = |1, 1\rangle|\frac{1}{2}, \frac{1}{2}\rangle$ *and that* $|\frac{1}{2}, -\frac{1}{2}\rangle = \frac{1}{\sqrt{3}}|1, 0\rangle|\frac{1}{2}, -\frac{1}{2}\rangle - \sqrt{\frac{2}{3}}|1, -1\rangle|\frac{1}{2}, \frac{1}{2}\rangle$ *it's easy to find* $\hat{S}^2_{1,-}|\psi\rangle = \sqrt{\frac{2}{3}} 2\hbar^2 |1, -1\rangle|\frac{1}{2}, \frac{1}{2}\rangle$ *and therefore* $\langle\psi|\hat{S}^2_{1,-}|\psi\rangle = -\frac{e^{-\mathrm{i}\phi_2}}{\sqrt{3}} \sqrt{\frac{2}{3}} \sqrt{\frac{2}{3}} 2\hbar^2 = -\frac{4\hbar^2}{3\sqrt{3}} e^{-\mathrm{i}\phi_2}$. *Having this average to be equal to* $\frac{4\hbar^2}{3\sqrt{3}}\mathrm{i}$ *we deduce that* $\phi_2 = \pi/2$. *In conclusion* $|\psi\rangle = \sqrt{\frac{2}{3}}\, |\frac{3}{2}, \frac{3}{2}\rangle + \frac{\mathrm{i}}{\sqrt{3}} |\frac{1}{2}, -\frac{1}{2}\rangle$.

4. A particle of spin $\frac{1}{2}$ and orbital angular momentum $l = 1$ rotates freely around the z axis being subject to the Hamiltonian

$$\hat{H} = \frac{\hat{L}_z^2}{2I}$$

where $\hat{L}_z$ is the z component of the its orbital angular momentum and I is the moment of inertia of the particle. The particle is prepared at time $t = 0$ in a simultaneous eigenstate of $\hat{J}^2$ and of $\hat{J}_z$ (where $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$ is the total angular momentum) with eigenvalues $\frac{3}{4}\hbar^2$ e $\frac{1}{2}\hbar$ respectively.

Determine at what times t^* the probability that a measurement of $\hat{J}^2$ give $\frac{15}{4}\hbar^2$ is maximum.
Solution *Based on the problem data the initial state is* $|\psi_0\rangle = |j, m_j\rangle_{ls} = |\frac{3}{2}, -\frac{1}{2}\rangle$ *with* $l = 1$ *and* $s = 1/2$. *To determine its temporal evolution we must write it as linear combination of the eigenkets of* $\hat{H}$, *which are of the form*

$|1, m\rangle|\frac{1}{2}, m_s\rangle$ *(with* $m = -1, 0, 1$ *and* $m_s = -\frac{1}{2}, \frac{1}{2}$*)* *a*nd which have energy eigenvalues $E_m = \frac{\hbar^2 m^2}{2I}$ *. From the theory of addition of angular momenta we have*

$$|\psi_0\rangle = |\frac{3}{2}, -\frac{1}{2}\rangle_{ls} = \frac{1}{\sqrt{3}}|1, 0\rangle|\frac{1}{2}, -\frac{1}{2}\rangle + \sqrt{\frac{2}{3}}|1, -1\rangle|\frac{1}{2}, \frac{1}{2}\rangle.$$

Therefore the ket at time t turns out to be

$$|\psi(t)\rangle = \frac{1}{\sqrt{3}}|1, 0\rangle|\frac{1}{2}, -\frac{1}{2}\rangle + \sqrt{\frac{2}{3}}|1, -1\rangle|\frac{1}{2}, \frac{1}{2}\rangle e^{\frac{i\hbar t}{2I}}$$

The probability $P(t)$ *that a measure of* $\hat{J}^2$ *provides the value* $\frac{3}{4}\hbar^2$ *at time t equals the probability that the system is (up to a phase factor) in the state*

$$|\frac{1}{2}, -\frac{1}{2}\rangle_{ls} = \sqrt{\frac{2}{3}}|1, 0\rangle|\frac{1}{2}, -\frac{1}{2}\rangle - \frac{1}{\sqrt{3}}|1, -1\rangle|\frac{1}{2}, \frac{1}{2}\rangle.$$

So

$$P(t) = |_{ls}\langle\frac{1}{2}, -\frac{1}{2}|\psi(t)\rangle|^2 = \left(\frac{\sqrt{2}}{3}\right)^2 |1 - e^{\frac{i\hbar t}{2I}}|^2 = \frac{8}{9}|\sin\left(\frac{\hbar t}{4I}\right)|^2.$$

This probability is maximized (and equals $P = \frac{8}{9}$*) at the times* t^* *for which* $\sin(\frac{\hbar t^*}{4I}) = \pm 1$*. Therefore*

$$t^* = \frac{4I\pi}{\hbar}\left(\frac{1}{2} + n\right)$$

with $n = 0, 1, 2\ldots$

5. The electron of a Hydrogen atom is found in the state

$$|\Psi\rangle = \frac{1}{\sqrt{2}}\ |1, 0, 0; +\rangle + \frac{1}{2}\ |2, 1, 1; -\rangle + \frac{i}{2}\ |2, 1, 0; +\rangle$$

where we use the shorthand notation $|n, l, m; \pm\rangle \equiv |n, l, m; \frac{1}{2}, \pm\frac{1}{2}\rangle$ for the autokets of principal quantum number n, angular momentum l, quantum azimuthal number m and spin projection along the zeta axis $\pm\hbar/2$.

i. What is the probability that a measure of the square of the total angular momentum $\hat{J}^2$ gives value $3\hbar^2/4$?

ii. Calculate the average value of the Hamiltonian $\hat{H} = \frac{\hat{p}^2}{2m} - \frac{e^2}{\hat{r}}$, i.e., $\langle\Psi|\hat{H}|\Psi\rangle$

iii. Calculate the average value of the radial coordinate, i.e $\langle\Psi|\hat{r}|\Psi\rangle$.

Solution *We denote by $|n, j, m_j\rangle$ the eigenkets with principal number n which are eigenkets of the square of the total angular momentum with eigenvalue $\hbar^2 j(j+1)$ and of the z component of the total angular momentum with eigenvalue $\hbar m_j$. From the theory of addition of angular momenta we have*

$$\begin{array}{ll}
|1, \tfrac{1}{2}, \tfrac{1}{2}\rangle = |1, 0, 0; +\rangle & \quad |1, 0, 0; +\rangle = |1, \tfrac{1}{2}, \tfrac{1}{2}\rangle \\
|2, \tfrac{3}{2}, \tfrac{1}{2}\rangle = \tfrac{1}{\sqrt{3}}|2, 1, 1; -\rangle + \sqrt{\tfrac{2}{3}}|2, 1, 0; +\rangle & \Rightarrow |2, 1, 0; +\rangle = \sqrt{\tfrac{2}{3}}|2, \tfrac{3}{2}, \tfrac{1}{2}\rangle - \tfrac{1}{\sqrt{3}}|2, \tfrac{1}{2}, \tfrac{1}{2}\rangle \\
|2, \tfrac{1}{2}, \tfrac{1}{2}\rangle = \sqrt{\tfrac{2}{3}}|2, 1, 1; -\rangle - \tfrac{1}{\sqrt{3}}|2, 1, 0; +\rangle & \quad |2, 1, 1; -\rangle = \tfrac{1}{\sqrt{3}}|2, \tfrac{3}{2}, \tfrac{1}{2}\rangle + \sqrt{\tfrac{2}{3}}|2, \tfrac{1}{2}, \tfrac{1}{2}\rangle
\end{array}$$

Therefore the state $|\Psi\rangle$ can also be written as

$$|\Psi\rangle = \frac{1}{\sqrt{2}}|1, \frac{1}{2}, \frac{1}{2}\rangle + \frac{1}{2\sqrt{3}}(1 + \mathrm{i}\sqrt{2})|2, \frac{3}{2}, \frac{1}{2}\rangle + \frac{1}{2\sqrt{3}}(\sqrt{2} - \mathrm{i})|2, \frac{1}{2}, \frac{1}{2}\rangle$$

i. The required probability is given by the sum of the probabilities of finding the particle in the state $|1, \frac{1}{2}, \frac{1}{2}\rangle$ or in the state $|2, \frac{1}{2}, \frac{1}{2}\rangle$. So $P = 3/4$.
ii. The eigenvalues of the Hamiltonian are $E_n = -\frac{e^2}{2n^2 a_B}$. We then have $\langle\Psi|\hat{H}|\Psi\rangle = -\frac{e^2}{2a_B}(\frac{1}{2} + \frac{1}{2}\frac{1}{4}) = -\frac{5e^2}{16a_B}$.
iii. Using the orthonormality of spherical harmonics we have

$$\begin{aligned}
\langle\Psi|\hat{r}|\Psi\rangle &= \int_0^\infty dr\, r^3 \frac{1}{2}\Big(R_{1,0}^2(r) + R_{2,1}^2(r)\Big) \\
&= \frac{1}{2}\int_0^\infty dr\, r^3\Big(\frac{4}{a_B^3}e^{-2r/a_B} + \frac{1}{24a_B^3}\frac{r^2}{a_B^2}e^{-r/a_B}\Big) \\
&= \frac{a_B}{2}\int dx\Big(\frac{x^3}{4} + \frac{x^5}{24}\Big)e^{-x} = \frac{a_B}{2}\Big(\frac{3!}{4} + \frac{5!}{24}\Big) = \frac{13}{4}a_B \qquad (5.104)
\end{aligned}$$

6. The ket $|\Psi\rangle$ describing a spin 1/2 particle in three dimensions has radial part fixed while the angular and spin part are described by the Hamiltonian $\hat{H} = \frac{2\varepsilon}{\hbar^2}\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}$ where $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ are the angular momentum and spin operators while ε is a constant with the dimensions of energy.
i. Taking into account that the possible eigenvalues of $\hat{L}^2$ are $\hbar^2 l(l+1)$ write the possible eigenvalues of $\hat{H}$ in terms of l
ii. Knowing that

- An energy measurement gives the value ε with probability 1/2 e the value -2ε with probability 1/2
- A measure of the observable J_z (z component total angular momentum) gives the value $-\frac{3}{2}\hbar$ with probability 1/2 and the value $\frac{1}{2}\hbar$ with probability 1/2
- The average value $\langle\Psi|\hat{J}_+\hat{S}_z\hat{J}_+|\Psi\rangle = \frac{\mathrm{i}}{\sqrt{6}}\hbar^3$

determine the ket $|\Psi\rangle$.

Solution *i. The Hamiltonian can also be written as* $\hat{H} = \frac{\varepsilon}{\hbar^2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2)$. *Taking into account that the particle has spin* $1/2$ *the total angular momentum for a given* l *can be* $j = l + \frac{1}{2}$ *or* $j = l - \frac{1}{2}$ *(the latter case only if* $l > 0$*). I*t follows that for a given l *the possible eigenvalues of* $\hat{H}$ *are*

$$E_l^{(+)} = \varepsilon[(l + \frac{1}{2})(l + \frac{1}{2} + 1) - l(l + 1) - \frac{3}{4}] = \varepsilon l \qquad \text{se } j = l + \frac{1}{2}$$

$$E_l^{(-)} = \varepsilon[(l - \frac{1}{2})(l - \frac{1}{2} + 1) - l(l + 1) - \frac{3}{4}] = -\varepsilon(l + 1) \qquad \text{se } j = l - \frac{1}{2}$$

ii. Based on the results of point i. from the first information we see that the ket $|\Psi\rangle$ *must have* $l = 1$ *with probability* $1/2$ *of having* $j = l + \frac{1}{2} = \frac{3}{2}$ *and probability* $1/2$ *of having* $j = l - \frac{1}{2} = \frac{1}{2}$*. So*

$$|\Psi\rangle = \frac{1}{\sqrt{2}}\sum_m a_m|\frac{3}{2}, m\rangle_{1,\frac{1}{2}} + \frac{1}{\sqrt{2}}\sum_m b_m|\frac{1}{2}, m\rangle_{1,\frac{1}{2}}$$

with $\sum_m |a_m|^2 = 1$ *and* $\sum_m |b_m|^2 = 1$*. The probability that a measurement of* J_z *gives* $-\frac{3}{2}\hbar$ *is equal to* $\frac{1}{2}|a_{-3/2}|^2$*. So, based on the second information* $|a_{-3/2}| = 1$*, which implies* $a_{3/2} = a_{1/2} = a_{-1/2} = 0$ *by virtue of normalization. Instead the probability that a measurement of* J_z *provides* $\frac{1}{2}\hbar$ *is equal to* $\frac{1}{2}|a_{1/2}|^2 + \frac{1}{2}|b_{1/2}|^2 = \frac{1}{2}|b_{1/2}|^2$ *being* $a_{1/2} = 0$*. Again based on the second piece of information we deduce that* $|b_{1/2}| = 1$ *and therefore* $b_{-1/2} = 0$ *by virtue of normalization. The searched state can therefore be written as* $|\Psi\rangle = \frac{1}{\sqrt{2}}|\frac{3}{2}, -\frac{3}{2}\rangle_{1,\frac{1}{2}} + \frac{e^{i\theta}}{\sqrt{2}}|\frac{1}{2}, \frac{1}{2}\rangle_{1,\frac{1}{2}}$*. To determine the phase* $e^{\mathrm{i}\theta}$ *we use the last information. It turns out that*

$$\begin{aligned}
\hat{S}_z\hat{J}_+|\Psi\rangle &= \frac{1}{\sqrt{2}}\hat{S}_z\hat{J}_+|\frac{3}{2}, -\frac{3}{2}\rangle_{1,\frac{1}{2}} \\
&= \frac{1}{\sqrt{2}}\hat{S}_z(\hat{L}_+ + \hat{S}_+)|1, -1\rangle|-\rangle = \frac{\hbar}{\sqrt{2}}\hat{S}_z\big(\sqrt{2}|1, 0\rangle|-\rangle + |1, -1\rangle|+\rangle\big) \\
&= -\frac{\hbar^2}{2}\big(|1, 0\rangle|-\rangle - \frac{1}{\sqrt{2}}|1, -1\rangle|+\rangle\big)
\end{aligned}$$

$$\hat{J}_-|\Psi\rangle = \frac{e^{\mathrm{i}\theta}}{\sqrt{2}}\hat{J}_-|\frac{1}{2}, \frac{1}{2}\rangle_{1,\frac{1}{2}} = \hbar\frac{e^{\mathrm{i}\theta}}{\sqrt{2}}|\frac{1}{2}, -\frac{1}{2}\rangle_{1,\frac{1}{2}} = \hbar\frac{e^{\mathrm{i}\theta}}{\sqrt{2}}\Big(\sqrt{\frac{2}{3}}|1, -1\rangle|+\rangle - \frac{1}{\sqrt{3}}|1, 0\rangle|-\rangle\Big)$$

So $\langle\Psi|\hat{J}_+\hat{S}_z\hat{J}_+|\Psi\rangle = \hbar^3\frac{e^{-\mathrm{i}\theta}}{\sqrt{6}}$*. Using the last information we then deduce that* $e^{\mathrm{i}\theta} = -\mathrm{i}$.

7. A particle of angular momentum $l = 2$ and spin $s = 1$ is described by the Hamiltonian

$$\hat{H} = E_0\left(\frac{\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}}{\hbar^2} + \frac{\hat{J}_z\hat{L}^2}{2\hbar^3}\right)$$

where $\hat{\mathbf{L}}$ are the angular momentum operators, $\hat{\mathbf{S}}$ are the spin operators and $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$.
i. Determine the eigenvalues of $\hat{H}$ and the corresponding degeneracy
ii. Indicating with $|j, m_j\rangle$ the eigenkets of the total angular momentum calculate the following matrix elements

$$\langle 3,3|\big[\hat{H},\hat{J}_+\big]|3,2\rangle, \qquad \langle 3,3|\big[\hat{H},\hat{J}_+\big]|2,2\rangle, \qquad \langle 3,3|\big[\hat{H},\hat{J}^2\big]|3,3\rangle, \qquad \langle 3,3|\hat{J}_+\hat{J}_-|3,3\rangle$$

Solution *We rewrite the Hamiltonian as* $\hat{H} = \frac{E_0}{2\hbar^2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2 + \frac{1}{\hbar}\hat{J}_z\hat{L}^2)$. *The eigenkets of the total angular momentum are* $|j, m_j\rangle$ *with* $j = 1, 2, 3$ *and* $m_j = -j, \ldots, j$. *The kets are also eigenkets of* $\hat{H}$:

$$\hat{H}|j, m_j\rangle = E_0\frac{j(j+1) - 8 + 6m_j}{2}|j, m_j\rangle$$

If $j = 3$ *we have the eigenvalues* $11E_0, 8E_0, 5E_0, 2E_0, -E_0, -4E_0, -7E_0, -7E_0$ *for* $m_j = 3,\ 2,\ 1, 0,\ -1,\ -2,\ -3$. *If* $j = 2$ *we have the eigenvalues*
$5E_0, 2E_0, -E_0, -4E_0, -7E_0$ *for* $m_j = 2,\ 1,\ 0,\ -1,\ -2$. *Finally if* $j = 1$ *we have the eigenvalues* $0, -3E_0, -6E_0$ *for* $m_j = 1, 0, -1$. *Therefore the eigenvalues* $5E_0, 2E_0, -E_0, -4E_0, -7E_0$ *have degeneracy 2 and all the others are degenerate only once.*
We now come to the calculation of the matrix elements. Using that $[\hat{J}_z, \hat{J}_+] = \hbar\hat{J}_+$ *it follows that* $[\hat{H}, \hat{J}_+] = \frac{E_0}{2\hbar^2}\hat{J}_+\hat{L}^2$. *We have*

$$\hat{J}_+\hat{L}^2|3,2\rangle = 6\hbar^3\sqrt{12-6}|3,3\rangle = 6\sqrt{6}\hbar^3|3,3\rangle.$$

Therefore $\langle 3,3|\big[\hat{H},\hat{J}_+\big]|3,2\rangle = 3\sqrt{6}E_0\hbar$. *The second matrix element is null since the operator* $[\hat{H}, \hat{J}_+]$ *does not change the quantum number* j. *The third matrix element is null since* $\hat{H}$ *commutes with* $\hat{J}^2$. *Finally for the last matrix element we have* $\hat{J}_+\hat{J}_- = (\hat{J}_x + \mathrm{i}\hat{J}_y)(\hat{J}_x - \mathrm{i}\hat{J}_y) = \hat{J}_x^2 + \hat{J}_y^2 - \mathrm{i}[\hat{J}_x, \hat{J}_y] = \hat{J}^2 - \hat{J}_z^2 + \hbar\hat{J}_z$. *Therefore* $\langle 3,3|\hat{J}_+\hat{J}_-|3,3\rangle = 6\hbar^2$.

8. A particle of spin $s = 1$ and angular momentum $l = 1$ is found in the following non-normalized state

$$|\psi\rangle = (\sqrt{2} + \mathrm{i})|1,1;1,1\rangle - \sqrt{2}|1,1;1,0\rangle + \sqrt{2}(1+\mathrm{i})|1,0;1,1\rangle$$

where the states $|l, m_l; s, m_s\rangle$ are eigenkets of $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$ and $\hat{S}_z$.
i. Normalize the state

ii. Tell what are the possible values of a measure of $\hat{J}^2 = (\hat{\mathbf{L}} + \hat{\mathbf{S}}) \cdot (\hat{\mathbf{L}} + \hat{\mathbf{S}})$ and calculate the probability of measuring them
iii. Calculate the average value of $\hat{J}^2$ and $\hat{J}_x$.
Solution *The norm of the state is 3. In the basis of the total angular momentum* $|j, m_j\rangle$ *the normalized state is written as*

$$\begin{aligned}|\psi\rangle &= \frac{1}{3}\left[(\sqrt{2}+i)|2,2\rangle - \sqrt{2}\frac{1}{\sqrt{2}}(|2,1\rangle + |1,1\rangle) + \sqrt{2}(1+i)\frac{1}{\sqrt{2}}(|2,1\rangle - |1,1\rangle)\right] \\ &= \frac{1}{3}\left[(\sqrt{2}+i)|2,2\rangle + i|2,1\rangle - (2+i)|1,1\rangle\right]\end{aligned}$$

The possible values of a measure of $\hat{J}^2$ *are* $6\hbar^2$, $2\hbar^2$ *and* 0 *and for our state the probabilities of measuring them are* $P(6\hbar^2) = 4/9$, $P(2\hbar^2) = 5/9$ *and* $P(0) = 0$.
To calculate the average values have

$$\langle\psi|\hat{J}^2|\psi\rangle = \frac{4}{9}6\hbar^2 + \frac{5}{9}2\hbar^2 = \frac{34}{9}\hbar^2$$

$$\langle\psi|\hat{J}_x|\psi\rangle = \frac{1}{2}\langle\psi|\hat{J}_+ + \hat{J}_-|\psi\rangle = \frac{2\sqrt{2}}{9}\hbar$$

9. Consider two electrons of spin 1/2 described by the Hamiltonian

$$\hat{H} = \epsilon\Big(\frac{\hat{J}^2}{\hbar^2} + \frac{\hat{J}_x}{\hbar}\Big)$$

where $\hat{\mathbf{J}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2$ with $\hat{\mathbf{S}}_1$ is the vector of spin operators of the first particle is $\hat{\mathbf{S}}_2$ is the vector of spin operators of the second particle. Ignoring the spatial part a possible basis of the Hilbert space for the spin part is $|\frac{1}{2}, m_1\rangle|\frac{1}{2}, m_2\rangle$ with $m_1 = \pm\frac{1}{2}$ and $m_2 = \pm\frac{1}{2}$ the projections of the spin along the z axis of the first and second particles respectively.
i. Find eigenvalues and eigenvectors of $\hat{H}$.
ii. Calculate the probability at time t that a measurement of $\hat{S}_{2,z}$ provides the value $-\hbar/2$ if at time zero system is in the state $|\Psi(0)\rangle = |\frac{1}{2}, \frac{1}{2}\rangle|\frac{1}{2}, -\frac{1}{2}\rangle$.

Solution *We introduce the compact notation* $|s_1 s_2\rangle$ *to denote the states* $|\frac{1}{2}, s_1\frac{1}{2}\rangle|\frac{1}{2}, s_2\frac{1}{2}\rangle$ *with* $s_1 = \pm$ *and* $s_2 = \pm$. *In the basis of total angular momentum we have the triplet states* $|1,1\rangle = |++\rangle$, $|1,0\rangle = \frac{1}{\sqrt{2}}\Big(|+-\rangle + |-+\rangle\Big)$, $|1,-1\rangle = |--\rangle$ *and the singlet state* $|0,0\rangle = \frac{1}{\sqrt{2}}\Big(|+-\rangle - |-+\rangle\Big)$.
i. The Hamiltonian commutes with $\hat{J}^2$ *and we can therefore find simultaneous eigenkets of* $\hat{J}^2$ *and* $\hat{H}$. *In the triplet space the matrix* $\mathbb{H}$ *of elements* $H_{mn} \equiv \langle 1, m|\hat{H}|1, n\rangle$ *is*

$$\mathbb{H} = \epsilon \begin{pmatrix} 2 & 1/\sqrt{2} & 0 \\ 1/\sqrt{2} & 2 & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & 2 \end{pmatrix}$$

The eigenvalues and eigenvectors are $E_1^T = \epsilon$ *with* $\psi_1 = \frac{1}{2}\begin{pmatrix} 1 \\ -\sqrt{2} \\ 1 \end{pmatrix}$; $E_2^T = 2\epsilon$ with $\psi_2 = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$; $E_3^T = 3\epsilon$ with $\psi_3 = \frac{1}{2}\begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix}$. *In the singlet space the matrix* $\mathbb{H} = 0$ *and therefore the singlet eigenvalue is* $E^S = 0$.
ii. In the basis of the total angular momentum the initial state is written like

$$|\Psi(0)\rangle = \frac{1}{\sqrt{2}}\Big(|1,0\rangle + |0,0\rangle\Big) = \frac{1}{\sqrt{2}}\Big(\frac{|\psi_3\rangle - |\psi_1\rangle}{\sqrt{2}} + |0,0\rangle\Big)$$

Therefore the state at time t turns out to be

$$|\Psi(t)\rangle = \frac{1}{\sqrt{2}}\Big(\frac{e^{\mathrm{i}3\epsilon t/\hbar}|\psi_3\rangle - e^{\mathrm{i}\epsilon t/\hbar}|\psi_1\rangle}{\sqrt{2}} + |0,0\rangle\Big)$$

The required probability is then

$$\begin{aligned} P(t) &= \Big|\langle + - |\Psi(t)\rangle\Big|^2 + \Big|\langle - - |\Psi(t)\rangle\Big|^2 = \frac{1}{2}\Big|\langle 1,0|\Psi(t)\rangle + \langle 0,0|\Psi(t)\rangle\Big|^2 + \Big|\langle 1,-1|\Psi(t)\rangle\Big|^2 \\ &= \frac{1}{2}\Big|\frac{1}{2}\frac{e^{\mathrm{i}3\epsilon t/\hbar}}{\sqrt{2}} + \frac{1}{2}\frac{e^{\mathrm{i}\epsilon t/\hbar}}{\sqrt{2}} + \frac{1}{\sqrt{2}}\Big|^2 + \frac{1}{2}\Big|\frac{e^{\mathrm{i}3\epsilon t/\hbar}}{2\sqrt{2}} - \frac{e^{\mathrm{i}\epsilon t/\hbar}}{2\sqrt{2}}\Big|^2 \\ &= \frac{1}{4}\Big|e^{2\mathrm{i}\epsilon t/\hbar}\cos(\epsilon t/\hbar) + 1\Big|^2 + \frac{1}{4}\sin^2(\epsilon t/\hbar) = \frac{1}{2}\Big(1 + \cos(\epsilon t/\hbar)\cos(2\epsilon t/\hbar)\Big) \end{aligned}$$

10. A particle of angular momentum $l = 1$ and spin $s = 1/2$ is described by the ket

$$|\Psi\rangle = Ce^{\frac{\mathrm{i}}{\hbar}\hat{L}_+}|1,-1\rangle|+\rangle$$

where $|1,m\rangle|\pm\rangle$ are the simultaneous eigenkets of $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$ and $\hat{S}_z$.
i. Calculate the normalization constant C
ii. Calculate the probability that a measurement of the total angular momentum provides the value $j = 1/2$.

Solution *i. Since* $l = 1$ *we can truncate the expansion of the exponential at the second order. We have*

$$|\Psi\rangle = C\Big(1 + \frac{\mathrm{i}}{\hbar}\hat{L}_+ - \frac{1}{2\hbar^2}\hat{L}_+^2\Big)|1,-1\rangle|+\rangle = C\Big(|1,-1\rangle|+\rangle + \mathrm{i}\sqrt{2}|1,0\rangle|+\rangle - |1,1\rangle|+\rangle\Big)$$

Therefore the normalization constant is $C = 1/2$.
ii. In the basis of the total angular momentum $|j, m_j\rangle$ *results* $|\frac{3}{2}, \frac{3}{2}\rangle = |1, 1\rangle|+\rangle$. *Applying* $\hat{J}_- = \hat{L}_- + \hat{S}_-$ *we find*

$$|\frac{3}{2}, \frac{1}{2}\rangle = \sqrt{\frac{2}{3}}|1, 0\rangle|+\rangle + \frac{1}{\sqrt{3}}|1, 1\rangle|-\rangle \quad \Rightarrow \quad |\frac{1}{2}, \frac{1}{2}\rangle = \frac{1}{\sqrt{3}}|1, 0\rangle|+\rangle - \sqrt{\frac{2}{3}}|1, 1\rangle|-\rangle$$

from which $|1.0\rangle|+\rangle = \frac{1}{\sqrt{3}}|\frac{1}{2}, \frac{1}{2}\rangle + \sqrt{\frac{2}{3}}|\frac{3}{2}, \frac{1}{2}\rangle$. *Applying again* $\hat{J}_- = \hat{L}_- + \hat{S}_-$ *to the state* $|\frac{3}{2}, \frac{1}{2}\rangle$ *we find*

$$|\frac{3}{2}, -\frac{1}{2}\rangle = \frac{1}{\sqrt{3}}|1, -1\rangle|+\rangle + \sqrt{\frac{2}{3}}|1, 0\rangle|-\rangle \quad \Rightarrow \quad |\frac{1}{2}, -\frac{1}{2}\rangle = \sqrt{\frac{2}{3}}|1, -1\rangle|+\rangle - \frac{1}{\sqrt{3}}|1, 0\rangle|-\rangle$$

from which $|1, -1\rangle|+\rangle = \frac{1}{\sqrt{3}}|\frac{3}{2}, -\frac{1}{2}\rangle + \sqrt{\frac{2}{3}}|\frac{1}{2}, -\frac{1}{2}\rangle$. *Substituting these results into* $|\Psi\rangle$ *we find*

$$|\Psi\rangle = \frac{1}{2}\left\{ -|\frac{3}{2}, \frac{3}{2}\rangle + \frac{2\mathrm{i}}{\sqrt{3}}|\frac{3}{2}, \frac{1}{2}\rangle - \frac{1}{\sqrt{3}}|\frac{3}{2}, \frac{1}{2}\rangle + \mathrm{i}\sqrt{\frac{2}{3}}|\frac{1}{2}, \frac{1}{2}\rangle - \sqrt{\frac{2}{3}}|\frac{1}{2}, -\frac{1}{2}\rangle \right\}$$

Therefore the required probability is $P(j = 1/2) = 1/3$.

11. Let $\hat{\mathbf{S}}_1 = (\hat{S}_{1,x}, \hat{S}_{1,y}, \hat{S}_{1,z})$ and $\hat{\mathbf{S}}_2 = (\hat{S}_{2,x}, \hat{S}_{2,y}, \hat{S}_{2,z})$ be the spin operators of two particles of spin 1/2. The particles are in the singlet state $|\Psi\rangle = \frac{1}{\sqrt{2}}\Big(|+, -\rangle - |-, +\rangle\Big)$ where "+" and " −" indicate that the spin projection along the z axis have values $+\hbar/2$ and $-\hbar/2$ respectively.
i. Calculate the square of the variance of the operators $\hat{S}_{1,x}$ and $\hat{S}_{1,y}$ and verify that the Heisenberg uncertainty principle is satisfied, i.e., $\langle\hat{\sigma}^2_{S_{1,x}}\rangle\langle\hat{\sigma}^2_{S_{1,y}}\rangle \geq \frac{1}{4}|\langle[\hat{S}_{1,x}, \hat{S}_{1,y}]\rangle|^2$.
ii. Determine the average value $\langle\hat{S}_2^2\rangle$.
iii. Let the Hamiltonian be given by $\hat{H} = \lambda\hat{S}_{1,z}$. Calculate the probability that a measure of the square of the total spin, i.e $\hat{S}^2 = (\hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2) \cdot (\hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2)$ provides the value $2\hbar^2$.
Solution *i. We write* $\hat{S}_{1,x} = \frac{1}{2}(\hat{S}_{1,+} + \hat{S}_{1,-})$ *and* $\hat{S}_{1,y} = \frac{1}{2\mathrm{i}}(\hat{S}_{1,+} - \hat{S}_{1,-})$. *We then have*

$$\begin{aligned}
\hat{S}_{1,x}|\Psi\rangle &= \frac{\hbar}{2\sqrt{2}}\Big(|-, -\rangle - |+, +\rangle\Big) \\
\hat{S}_{1,y}|\Psi\rangle &= -\frac{\hbar}{2\mathrm{i}\sqrt{2}}\Big(|-, -\rangle + |+, +\rangle\Big) \\
\hat{S}_{1,z}|\Psi\rangle &= \frac{\hbar}{2\sqrt{2}}\Big(|+, -\rangle + |-, +\rangle\Big)
\end{aligned}$$

and therefore $\langle\Psi|\hat{S}_{1,x}|\Psi\rangle = \langle\Psi|\hat{S}_{1,y}|\Psi\rangle = \langle\Psi|\hat{S}_{1,z}|\Psi\rangle = 0$. *We also have*

$$\hat{S}^2_{1,x}|\Psi\rangle = \hat{S}^2_{1,y}|\Psi\rangle = \hat{S}^2_{1,z}|\Psi\rangle = \frac{\hbar^2}{4}|\Psi\rangle.$$

It follows that $\langle\hat{\sigma}^2_{S_{1,x}}\rangle\langle\hat{\sigma}^2_{S_{1,y}}\rangle = \hbar^4/16$. *Since* $[\hat{S}_{1,x}, \hat{S}_{1,y}] = \mathrm{i}\hbar\hat{S}_{1,z}$ *we also have* $\langle[\hat{S}_{1,x}, \hat{S}_{1,y}]\rangle = 0$. *Therefore the Heisenberg uncertainty principle is satisfied.*
ii. The singlet state is a simultaneous eigenket of $\hat{S}_1^2$, $\hat{S}_2^2$, $\hat{S}^2$ *and* $\hat{S}_z$ *where* $\hat{\mathbf{S}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2$. *Therefore* $\langle\hat{S}_2^2\rangle = 3\hbar^2/4$.
iii. At time t the ket of the system is given by

$$|\Psi(t)\rangle = e^{-\mathrm{i}\hat{H}t/\hbar}|\Psi\rangle = \frac{1}{\sqrt{2}}\Big(e^{-\mathrm{i}\lambda t/2}|+,-\rangle - e^{\mathrm{i}\lambda t/2}|-,+\rangle\Big)$$
$$= \frac{e^{-\mathrm{i}\lambda t/2}}{\sqrt{2}}\Big(|+,-\rangle - e^{\mathrm{i}\lambda t}|-,+\rangle\Big).$$

Since this state is always orthogonal to $|+,+\rangle$ *and* $|-,-\rangle$ *the required probability is given by*

$$P(t) = \left|\frac{1}{\sqrt{2}}\Big(\langle+,-| + \langle-,+|\Big)|\Psi(t)\rangle\right|^2 = \frac{1}{4}|1 - e^{\mathrm{i}\lambda t}|^2 = \frac{1}{2}(1 - \cos\lambda t).$$

12. Consider a spin 1/2 particle in three dimensions. At time $t = 0$ a simultaneous measurement of the operators

$$\hat{A} \equiv \hat{L}^2, \qquad \hat{B} \equiv \hat{L}^2_+ + \hat{L}^2_-, \quad \hat{C} \equiv \hat{S}_x$$

gives the values $a = 2\hbar^2$, $b = 2\hbar^2$ and $c = \hbar/2$ respectively. Knowing that the particle is governed by the Hamiltonian $\hat{H} = \frac{\varepsilon}{\hbar}\hat{S}_z$
i. Write the ket of the particle at time t
ii. Calculate the probability at time t that a measure of total angular momentum $\hat{J}^2$ provides the value $\frac{15}{4}\hbar^2$.
Solution *i. From the first piece of information we know that the particle collapses into the state with* $l = 1$. *In the subspace* $|1, m\rangle$ *the operator* $\hat{B}$ *has eigenvalues* $\pm 2\hbar^2$ *and 0, the eigenket with eigenvalue* $2\hbar^2$ *being* $\frac{1}{\sqrt{2}}\Big(|1,1\rangle + |1,-1\rangle\Big)$. *Finally the measurement of* $\hat{S}_x$ *uniquely determines the spin ket, i.e* $\frac{1}{\sqrt{2}}\Big(|+\rangle + |-\rangle\Big)$. *We conclude that after the simultaneous measurement of the three operators the particle collapses in the state* $|\Psi(0)\rangle = \frac{1}{2}\Big(|1,1\rangle + |1,-1\rangle\Big)\Big(|+\rangle + |-\rangle\Big)$. *The time evolution is therefore given by*

$$|\Psi(t)\rangle = \frac{1}{2}\Big(|1,1\rangle + |1,-1\rangle\Big)\Big(e^{-\mathrm{i}\frac{\varepsilon t}{2\hbar}}|+\rangle + e^{\mathrm{i}\frac{\varepsilon t}{2\hbar}}|-\rangle\Big)$$

ii. To determine the required probability it is necessary to calculate $P(j = 3/2, t) = \sum_m |\langle \frac{3}{2}, m|\Psi(t)\rangle|^2$. *From the theory of addition of angular momenta we know that*

$$\begin{aligned}
|\tfrac{3}{2},\tfrac{3}{2}\rangle &= |1,1\rangle|+\rangle\\
|\tfrac{3}{2},\tfrac{1}{2}\rangle &= \sqrt{\tfrac{2}{3}}|1,0\rangle|+\rangle + \tfrac{1}{\sqrt{3}}|1,1\rangle|-\rangle\\
|\tfrac{3}{2},-\tfrac{1}{2}\rangle &= \sqrt{\tfrac{2}{3}}|1,0\rangle|-\rangle + \tfrac{1}{\sqrt{3}}|1,-1\rangle|+\rangle\\
|\tfrac{3}{2},-\tfrac{3}{2}\rangle &= |1,-1\rangle|-\rangle
\end{aligned}$$

So $P(j = 3/2, t) = \frac{1}{4} + \frac{1}{12} + \frac{1}{12} + \frac{1}{4} = \frac{5}{12}$, *which is independent of time* t.

More Exercises

13. The Hamiltonian of a particle of spin $s = 1/2$ in three dimensions is given by

$$\hat{H} = \alpha\,\hat{\mathbf{p}}\cdot\hat{\mathbf{S}}\,.$$

Determine the eigenvalues and expand the eigenkets of $\hat{H}$ in the basis $|\mathbf{p}; s, m_s\rangle$ of the simultaneous eigenkets of the momentum operator $\hat{\mathbf{p}}$ and spin operators $\hat{S}^2$ and $\hat{S}_z$.

14. Determine the spin matrices $\mathbb{S}_x$, $\mathbb{S}_y$ and $\mathbb{S}_z$ for $s = 3/2$. Then calculate trace and determinant for the three spin matrices. Is it the same? If yes, justify the answer
15. A particle of mass m and spin $s = 1/2$ in one dimension is described by the following Hamiltonian

$$\hat{H} = \lambda\sqrt{\frac{m\omega}{2\hbar}}\hat{x}\hat{S}_y + \lambda\frac{1}{\sqrt{2m\hbar\omega}}\hat{p}\hat{S}_x$$

i. Calculate $\hat{H}^2$ (Hint: use that matrices of spin $s = 1/2$ are proportional to the Pauli matrices which satisfy $\sigma_i\sigma_j = \delta_{ij}\mathbb{1} + \mathrm{i}\sum_k \varepsilon_{ijk}\sigma_k$).
ii. Determine eigenkets and eigenvalues of $\hat{H}^2$.
iii. Determine eigenkets and eigenvalues of $\hat{H}$.

16. The electron of a Hydrogen atom is found in the state

$$|\Psi\rangle = \frac{|1,0,0;+\rangle + |2,1,1;-\rangle + |2,1,0;+\rangle}{\sqrt{3}}$$

where the shorthand notation has been used $|n, l, m; \pm\rangle \equiv |n, l, m; \frac{1}{2}, \pm\frac{1}{2}\rangle$ for the autokets of principal quantum number n, angular momentum l, quantum azimuthal number m and spin projection along the z axis $\pm\hbar/2$.
i. Calculate the average value of the spin along the z axis, i.e., $\hat{S}_z$.
ii. Calculate the average value of the Hamiltonian $\hat{H}$.
iii. Calculate the variance of the Hamiltonian

17. A particle of spin $s = \frac{1}{2}$ is in a state at time $t = 0$ with spin projection along the z axis equal to $\hbar/2$ and the angular dependence of the wavefunction is given by

$$\Psi(\theta, \phi) = N(\sin\theta\cos\phi + \sin\theta\sin\phi)$$

i. Calculate the normalization N and the expansion of Ψ in spherical harmonics with $l = 1$.
Calculate the time evolution of the initial state knowing that the Hamiltonian of the system is $\hat{H} = \frac{\alpha}{\hbar^2}\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$.
Calculate the average value of $\hat{J}^2 = (\hat{\mathbf{L}} + \hat{\mathbf{S}}) \cdot (\hat{\mathbf{L}} + \hat{\mathbf{S}})$ as a function of time.

Chapter 6
Approximation Methods

The problems that can be exactly solved in quantum mechanics can be counted on the fingers of one hand. They include problems with piecewise constant potentials, the harmonic oscillator, the hydrogen atom, and a few others. By "exactly solving a problem" here, we mean the exact diagonalization of the Hamiltonian operator, i.e., the calculation of its eigenvalues and eigenkets. In the vast majority of cases, exact diagonalization is extremely complicated. In this chapter, we see how to approach these cases using methods that allow us to approximate the exact solution.

6.1 Perturbation Theory: Correction to Energy Levels

Often, we encounter problems in which the Hamiltonian $\hat{H}$ is the sum of an operator $\hat{H}_0$ that we know how to exactly diagonalize and another operator $\hat{P}$, called the perturbation, which produces small corrections to the eigenvalues and eigenkets of $\hat{H}_0$:

$$\hat{H} = \hat{H}_0 + \hat{P}. \tag{6.1}$$

In such cases, it is possible to develop a method that allows us to calculate *perturbatively* the corrections due to the operator $\hat{P}$. In this chapter, we focus on developing such a method. Although we work to correct the eigenvalues and eigenkets of $\hat{H}_0$, the method is applicable in other contexts. If we are interested in diagonalizing the operator $\hat{C} = \hat{A} + \hat{B}$ and know the eigenvalues and eigenkets of $\hat{A}$, we can calculate the corrections due to $\hat{B}$ by simply replacing $\hat{H}_0$ with $\hat{A}$ and $\hat{P}$ with $\hat{B}$ in all the formulas that follow.

The idea behind the perturbation method is as follows. Consider the Hamiltonian:

$$\hat{H}_\lambda = \hat{H}_0 + \lambda \hat{P}, \tag{6.2}$$

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with λ a dimensionless parameter between 0 and 1. For $\lambda = 0$, the above Hamiltonian reduces to $\hat{H}_0$, while for $\lambda = 1$, the above Hamiltonian reduces to the one we are interested in, i.e., that of Eq. (6.1). As λ increases from $\lambda = 0$, the eigenvalues $E_n(\lambda)$ and eigenkets $|E_n(\lambda)\rangle$ of $\hat{H}_\lambda$ start from those of the unperturbed $\hat{H}_0$ and then deviate from them until becoming those of $\hat{H}$ when $\lambda = 1$. The perturbation method consists of expanding both the eigenvalues and eigenkets in power series of λ. By truncating these expansions at a certain power of λ and evaluating them at $\lambda = 1$, we obtain approximate results for eigenvalues and eigenkets.

6.1.1 *Correction to Nondegenerate Levels*

We here develop the theory for a non-degenerate eigenvalue of $\hat{H}_0$. Let us say that the relevant eigenvalue is that of the nth level

$$\hat{H}_0|E_n^{(0)}\rangle = E_n^{(0)}|E_n^{(0)}\rangle. \tag{6.3}$$

Our goal is to find the eigenvalue $E_n(\lambda)$ and the eigenket $|E_n(\lambda)\rangle$ that satisfy

$$\hat{H}_\lambda|E_n(\lambda)\rangle = E_n(\lambda)|E_n(\lambda)\rangle. \tag{6.4}$$

Let us expand the eigenvalues of $\hat{H}_\lambda$ in a power series of λ:

$$E_n(\lambda) = E_n^{(0)} + \Delta_n(\lambda) = E_n^{(0)} + \sum_{k=1}^{\infty} \lambda^k \Delta_n^{(k)}, \tag{6.5}$$

where we have taken into account that $E_n(\lambda = 0) = E_n^{(0)}$ and therefore the power series expansion of $\Delta_n(\lambda)$ starts from $k = 1$. Now we rewrite Eq. (6.4) using both the explicit form of $\hat{H}_\lambda$ and Eq. (6.5)

$$(\hat{H}_0 + \lambda\hat{P})|E_n(\lambda)\rangle = (E_n^{(0)} + \Delta_n)|E_n(\lambda)\rangle, \tag{6.6}$$

from which

$$(E_n^{(0)} - \hat{H}_0)|E_n(\lambda)\rangle = (\lambda\hat{P} - \Delta_n)|E_n(\lambda)\rangle. \tag{6.7}$$

Since the set of unperturbed eigenkets of $\hat{H}_0$ forms an orthonormal basis, we can expand the ket $|E_n(\lambda)\rangle$ in this basis

$$|E_n(\lambda)\rangle = |E_n^{(0)}\rangle + \sum_{m\neq n} c_m|E_m^{(0)}\rangle. \tag{6.8}$$

Note that the ket $|E_n(\lambda)\rangle$ is not normalized. In fact,

$$\langle E_n(\lambda)|E_n(\lambda)\rangle = 1 + \sum_{m\neq n} |c_m|^2 > 1. \tag{6.9}$$

We take care of normalizing it later. Substituting the expansion of Eq. (6.8) into the left-hand side of Eq. (6.7), we obtain

$$\sum_{m\neq n} c_m (E_n^{(0)} - E_m^{(0)})|E_m^{(0)}\rangle = (\lambda\hat{P} - \Delta_n)|E_n(\lambda)\rangle, \tag{6.10}$$

and bracketing with $\langle E_p^{(0)}|$ we can derive the following expression for the coefficients c_p

$$c_p = \frac{\langle E_p^{(0)}|\lambda\hat{P} - \Delta_n|E_n(\lambda)\rangle}{E_n^{(0)} - E_p^{(0)}}. \tag{6.11}$$

Substituting this result into the expansion of Eq. (6.8), we arrive at a recursive formula for the sought eigenket

$$|E_n(\lambda)\rangle = |E_n^{(0)}\rangle + \sum_{m\neq n} \frac{1}{E_n^{(0)} - E_m^{(0)}} |E_m^{(0)}\rangle\langle E_m^{(0)}|\lambda\hat{P} - \Delta_n|E_n(\lambda)\rangle. \tag{6.12}$$

To better recognize the recursion in this equation, we define the operator

$$\hat{\mathcal{I}}_n = \sum_{m\neq n} \frac{|E_m^{(0)}\rangle\langle E_m^{(0)}|}{E_n^{(0)} - E_m^{(0)}}. \tag{6.13}$$

Then Eq. (6.12) becomes

$$|E_n(\lambda)\rangle = |E_n^{(0)}\rangle + \hat{\mathcal{I}}_n(\lambda\hat{P} - \Delta_n)|E_n(\lambda)\rangle. \tag{6.14}$$

If now, in place of the ket $|E_n(\lambda)\rangle$ appearing on the right, we substitute the entire right-hand side (which is also equal to $|E_n(\lambda)\rangle$), we find

$$|E_n(\lambda)\rangle = |E_n^{(0)}\rangle + \hat{\mathcal{I}}_n(\lambda\hat{P} - \Delta_n)|E_n^{(0)}\rangle + \hat{\mathcal{I}}_n(\lambda\hat{P} - \Delta_n)\hat{\mathcal{I}}_n(\lambda\hat{P} - \Delta_n)|E_n(\lambda)\rangle \tag{6.15}$$

We can now continue iteratively and replace each occurrence of the ket $|E_n(\lambda)\rangle$ on the right with the entire right-hand side of Eq. (6.14):

$$\begin{aligned} |E_n(\lambda)\rangle &= |E_n^{(0)}\rangle + \hat{\mathcal{I}}_n(\lambda\hat{P} - \Delta_n)|E_n(\lambda)\rangle \\ &= |E_n^{(0)}\rangle + \hat{\mathcal{I}}_n(\lambda\hat{P} - \Delta_n)|E_n^{(0)}\rangle + \hat{\mathcal{I}}_n(\lambda\hat{P} - \Delta_n)\hat{\mathcal{I}}_n(\lambda\hat{P} - \Delta_n)|E_n^{(0)}\rangle + \dots \end{aligned} \tag{6.16}$$

In this way, we obtain an expansion of the ket $|E_n(\lambda)\rangle$ in terms of the unperturbed eigenkets of $\hat{H}_0$. Let $|E_n^{(k)}\rangle$ denote the term proportional to λ^k in this expansion, so

$$|E_n(\lambda)\rangle = \sum_{k=0}^{\infty} \lambda^k |E_n^{(k)}\rangle. \tag{6.17}$$

Using the power series expansion of λ in Eq. (6.5), we can identify the various $|E_n^{(k)}\rangle$:

$$\begin{aligned} |E_n^{(1)}\rangle &= \hat{\mathcal{I}}_n(\hat{P} - \Delta_n^{(1)})|E_n^{(0)}\rangle \\ |E_n^{(2)}\rangle &= \left[\hat{\mathcal{I}}_n(\hat{P} - \Delta_n^{(1)})\hat{\mathcal{I}}_n(\hat{P} - \Delta_n^{(1)}) - \hat{\mathcal{I}}_n\Delta_n^{(2)}\right]|E_n^{(0)}\rangle \\ &\ldots \end{aligned} \tag{6.18}$$

We have obtained expressions to correct the eigenket to a certain order in λ. However, these expressions require knowledge of $\Delta_n^{(k)}$. How to obtain these? Nothing simpler. Multiplying Eq. (6.7) by the bra $\langle E_n^{(0)}|$ we find

$$\langle E_n^{(0)}|(E_n^{(0)} - \hat{H}_0)|E_n(\lambda)\rangle = 0 = \langle E_n^{(0)}|(\lambda\hat{P} - \Delta_n)|E_n(\lambda)\rangle = \lambda\langle E_n^{(0)}|\hat{P}|E_n(\lambda)\rangle - \Delta_n, \tag{6.19}$$

where we take into account that, by virtue of Eq. (6.8), $\langle E_n^{(0)}|E_n(\lambda)\rangle = 1$ for every λ. Therefore,

$$\Delta_n = \lambda\langle E_n^{(0)}|\hat{P}|E_n(\lambda)\rangle. \tag{6.20}$$

Using the power series expansion of λ for both Δ_n (see Eq. (6.5)) and $|E_n(\lambda)\rangle$ (see Eq. (6.17)), and equating coefficients with the same powers, we find

$$\Delta_n^{(k)} = \langle E_n^{(0)}|\hat{P}|E_n^{(k-1)}\rangle. \tag{6.21}$$

So, based on the results in Eq. (6.18), we have for the first-order correction

$$\Delta_n^{(1)} = \langle E_n^{(0)}|\hat{P}|E_n^{(0)}\rangle, \tag{6.22}$$

for the second-order correction

$$\begin{aligned} \Delta_n^{(2)} &= \langle E_n^{(0)}|\hat{P}\hat{\mathcal{I}}_n(\hat{P} - \Delta_n^{(1)})|E_n^{(0)}\rangle = \langle E_n^{(0)}|\hat{P}\hat{\mathcal{I}}_n\hat{P}|E_n^{(0)}\rangle \\ &= \sum_{m\neq n} \frac{|\langle E_n^{(0)}|\hat{P}|E_m^{(0)}\rangle|^2}{E_n^{(0)} - E_m^{(0)}} \end{aligned} \tag{6.23}$$

and so on. Note that if the level in question is that of the ground state, then $E_n^{(0)} < E_m^{(0)}$ for every $m \neq n$, and therefore $\Delta_n^{(2)} < 0$. Thus, *the second-order correction to the energy of the ground state is always negative*.

6.1.2 *Correction to Degenerate Levels*

We now consider the case where the level to be corrected is a degenerate level with degeneracy $d > 1$. As usual, we denote by n the level in question, by $E_n^{(0)}$ its energy, and by $|E_{n,g}^{(0)}\rangle$ the degenerate eigenkets. Therefore

$$\hat{H}_0|E_{n,g}^{(0)}\rangle = E_n^{(0)}|E_{n,g}^{(0)}\rangle, \qquad g = 1, \ldots, d. \tag{6.24}$$

Our goal is to find the eigenvalues $E_{n,v}(\lambda)$ and the eigenkets $|E_{n,v}(\lambda)\rangle$ that satisfy

$$\hat{H}_\lambda|E_{n,v}(\lambda)\rangle = E_{n,v}(\lambda)|E_{n,v}(\lambda)\rangle, \qquad v = 1, \ldots, d, \tag{6.25}$$

where the eigenvalues $E_{n,v}(\lambda)$ calculated at $\lambda = 0$ all coincide with $E_n^{(0)}$. In general, there is no reason to expect that the perturbation $\lambda\hat{P}$ preserves the degeneracy of the level n, so we must consider the possibility that the perturbed energies are different from each other. This is why we have introduced an index, the index v specifically, to the energies. If the level no longer remains degenerate, and we anticipate that this happens in the majority of cases, we say that the level has undergone a **splitting** due to the perturbation.

Let us expand the perturbed energies $E_{n,v}(\lambda)$ in a power series of λ as we did in the non-degenerate case

$$E_{n,v}(\lambda) = E_n^{(0)} + \Delta_{n,v}(\lambda) = E_n^{(0)} + \sum_{k=1}^{\infty} \lambda^k \Delta_{n,v}^{(k)}. \tag{6.26}$$

Proceeding as before, it is straightforward to verify that Eq. (6.25) implies

$$(E_n^{(0)} - \hat{H}_0)|E_{n,v}(\lambda)\rangle = (\lambda\hat{P} - \Delta_{n,v})|E_{n,v}(\lambda)\rangle. \tag{6.27}$$

Since the set of unperturbed eigenkets of $\hat{H}_0$ forms an orthonormal basis, we can expand the kets $|E_{n,v}(\lambda)\rangle$ in this basis.

$$|E_{n,v}(\lambda)\rangle = \sum_g c_{v,g}|E_{n,g}^{(0)}\rangle + \sum_{m\neq n} c_m|E_m^{(0)}\rangle. \tag{6.28}$$

In this equation, the first sum is a linear combination of the degenerate kets, while the second sum is a combination of all the remaining kets. Substituting the expansion of Eq. (6.28) into the left-hand side of Eq. (6.27), we obtain

$$\sum_{m\neq n} c_m(E_n^{(0)} - E_m^{(0)})|E_m^{(0)}\rangle = (\lambda\hat{P} - \Delta_{n,v})|E_{n,v}(\lambda)\rangle, \tag{6.29}$$

and bracketing with $\langle E_p^{(0)}|$, we find the following expression for the coefficients c_p

$$c_p = \frac{\langle E_p^{(0)}|\lambda\hat{P} - \Delta_{n,v}|E_{n,v}(\lambda)\rangle}{E_n^{(0)} - E_p^{(0)}}. \tag{6.30}$$

Substituting this result into the expansion of Eq. (6.28), we arrive at a recursive formula for the sought eigenket

$$|E_{n,v}(\lambda)\rangle = \sum_g c_{v,g}|E_{n,g}^{(0)}\rangle + \sum_{m\neq n}\frac{1}{E_n^{(0)} - E_m^{(0)}}|E_m^{(0)}\rangle\langle E_m^{(0)}|\lambda\hat{P} - \Delta_{n,v}|E_{n,v}(\lambda)\rangle. \tag{6.31}$$

Unlike the non-degenerate case, if we knew $\Delta_{n,v}$, this recursive equation would not be sufficient to calculate $|E_{n,v}(\lambda)\rangle$. The reason is that we do not know the coefficients $c_{v,g}$. In the non-degenerate case, this problem did not arise because there was only one such coefficient, and we could choose its value to be 1 since normalization can always be fixed later. In the degenerate case, the condition of the normalization is not enough. It allows us to choose the value of one of the coefficients $c_{v,g}$, not all of them. Determining these coefficients (up to a multiplicative constant that can be fixed later with the normalization) is, however, rather simple. Multiplying Eq. (6.27) by the bra $\langle E_{n,g'}^{(0)}|$, we find

$$\lambda\langle E_{n,g'}^{(0)}|\hat{P}|E_{n,v}(\lambda)\rangle = \Delta_{n,v}c_{v,g'}\,. \tag{6.32}$$

This equation, together with Eq. (6.31), allows us to determine both the coefficients $c_{v,g}$ and the corrections $\Delta_{n,v}$ at all orders in λ. In the following, we explicitly work with the lowest order in λ.

The lowest order in λ of the quantity $\lambda\langle E_{n,g'}^{(0)}|\hat{P}|E_{n,v}(\lambda)\rangle$ is the first order, and it is obtained by approximating $|E_{n,v}(\lambda)\rangle$ with its expression at zeroth order in λ, i.e., with the first term on the right side of Eq. (6.31). Also, for the quantity $\Delta_{n,v}c_{v,g'}$, the lowest order in λ is the first order, and it is obtained by approximating $\Delta_{n,v}$ with $\lambda\Delta_{n,v}^{(1)}$, see Eq. (6.26). Equating the first-order terms in λ of Eq. (6.32), we find

$$\sum_g \langle E_{n,g'}^{(0)}|\hat{P}|E_{n,g}^{(0)}\rangle c_{v,g} = \Delta_{n,v}^{(1)}c_{v,g'}\,. \tag{6.33}$$

We recognize in this equation an eigenvalue equation. In fact, if we define the $d \times d$ matrix $\mathbb{P}$ with matrix elements

$$P_{g',g} = \langle E_{n,g'}^{(0)}|\hat{P}|E_{n,g}^{(0)}\rangle, \tag{6.34}$$

and the vector $\mathbf{c}_v$ of size d with components $c_{v,g}$, then we can rewrite Eq. (6.33) in matrix form as follows

$$\mathbb{P}\mathbf{c}_v = \Delta_{n,v}^{(1)}\mathbf{c}_v. \tag{6.35}$$

In conclusion, given the perturbation $\hat{P}$, the lowest-order corrections to the degenerate eigenvalue $E_n^{(0)}$ with degenerate eigenkets $|E_{n,g}^{(0)}\rangle$ are the eigenvalues $\Delta_{n,v}^{(1)}$ of the matrix $\mathbb{P}$, while the lowest-order eigenkets are given by

$$|E_{n,v}\rangle = \sum_g c_{v,g}|E_{n,g}^{(0)}\rangle \tag{6.36}$$

where the $c_{v,g}$ are the components of the eigenvector of $\mathbb{P}$ with eigenvalue $\Delta_{n,v}^{(1)}$.

6.2 Perturbation Theory: Time Evolution

The perturbative method described in the previous section allows for the approximate calculation of eigenvalues and eigenkets of operators given by the sum of an operator for which everything is known and a small perturbation. In this section, we want to develop a perturbative method that allows for the calculation of the time evolution of a ket, independent of the ket, when the Hamiltonian has the form

$$\hat{H}(t) = \hat{H}_0 + \hat{P}(t), \tag{6.37}$$

where the perturbation $\hat{P}(t)$ is an operator that can explicitly depend on time. As in the previous case, we assume that all the eigenvalues $E_n^{(0)}$ and eigenkets $|E_n^{(0)}\rangle$ of $\hat{H}_0$ are known. They can be either degenerate or non-degenerate; the derivation that follows does not depend on the degeneracy of the unperturbed levels. We introduce the operator

$$\hat{H}_\lambda = \hat{H}_0 + \lambda\hat{P}(t) \tag{6.38}$$

such that for $\lambda = 0$ it yields the Hamiltonian $\hat{H}_0$, while for $\lambda = 1$ it yields the Hamiltonian in Eq. (6.37). We expand all quantities in power series of λ. Approximate results are obtained by truncating these expansions at a certain order in λ and evaluating everything at $\lambda = 1$.

Given the ket $|\Psi_0\rangle$ at time $t = 0$, our intention is to approximately (or perturbatively in λ) solve the Schrödinger equation

$$\mathrm{i}\hbar\frac{d}{dt}|\Psi(t)\rangle = \left(\hat{H}_0 + \lambda\hat{P}(t)\right)|\Psi(t)\rangle. \tag{6.39}$$

To do this, we expand the ket $|\Psi(t)\rangle$ in the basis of the eigenkets of $\hat{H}_0$ as follows:

$$|\Psi(t)\rangle = \sum_n e^{-\frac{\mathrm{i}E_n^{(0)}t}{\hbar}} c_n(t)|E_n^{(0)}\rangle. \tag{6.40}$$

The initial condition $|\Psi(0)\rangle = |\Psi_0\rangle$ implies that

$$c_n(0) = \langle E_n^{(0)}|\Psi_0\rangle. \tag{6.41}$$

The reason why we have written the expansion coefficients as an exponential times the coefficients c_n is easily explained. When $\lambda = 0$, the ket $|\Psi(t)\rangle$ with $c_n(t) = c_n(0)$ constant in time solves the Schrödinger equation, see Eq. (1.148). Therefore, the time dependence of the c_n is due to the presence of the perturbation and provides information about its nature and how relevant it is. Substituting Eq. (6.40) into Eq. (6.39) yields

$$\sum_n e^{-\frac{iE_n^{(0)}t}{\hbar}} i\hbar \frac{dc_n(t)}{dt}|E_n^{(0)}\rangle = \lambda \sum_n e^{-\frac{iE_n^{(0)}t}{\hbar}} \hat{P}(t)c_n(t)|E_n^{(0)}\rangle \tag{6.42}$$

Multiplying both sides of this equation by $\langle E_m^{(0)}|e^{\frac{iE_m^{(0)}t}{\hbar}}$ and defining the frequencies

$$\Omega_{mn} = \frac{E_m^{(0)} - E_n^{(0)}}{\hbar} \tag{6.43}$$

we find a system of differential equations for the coefficients $\{c_n\}$

$$i\hbar \frac{dc_m(t)}{dt} = \lambda \sum_n \langle E_m^{(0)}|\hat{P}(t)|E_n^{(0)}\rangle e^{i\Omega_{mn}t} c_n(t). \tag{6.44}$$

Defining the time-dependent matrix $\mathbb{P}(t)$ with matrix elements

$$P_{mn}(t) = \langle E_m^{(0)}|\hat{P}(t)|E_n^{(0)}\rangle = P_{nm}^*(t) \tag{6.45}$$

and integrating Eq. (6.44) with respect to time, we arrive at a recursive equation for the coefficients $\{c_n\}$:

$$c_m(t) = c_m(0) - \frac{i\lambda}{\hbar} \sum_n \int_0^t dt' P_{mn}(t') e^{i\Omega_{mn}t'} c_n(t'). \tag{6.46}$$

This equation allows us to expand the coefficients in a power series of λ. In fact, rewriting the equation above for $c_n(t')$ instead of $c_m(t)$ and then substituting under the integral sign in Eq. (6.46), we have

$$\begin{aligned} c_m(t) &= c_m(0) - \frac{i\lambda}{\hbar} \sum_n \int_0^t dt' P_{mn}(t') e^{i\Omega_{mn}t'} c_n(0) \\ &+ \left(\frac{i\lambda}{\hbar}\right)^2 \sum_{nn'} \int_0^t dt' P_{mn}(t') e^{i\Omega_{mn}t'} \int_0^{t'} dt'' P_{nn'}(t'') e^{i\Omega_{nn'}t''} c_{n'}(t''). \end{aligned} \tag{6.47}$$

Continuing to iterate, we generate the power series in λ. It is important to realize that up to this point, no approximation has been made. In this book, we only study the first-order approximation in λ. This means that we approximate $c_m(t)$ with the first row of Eq. (6.47).

The first-order formula is further simplified in the case where the ket at time $t = 0$ is an eigenket of $\hat{H}_0$, i.e., $|\Psi_0\rangle = |E_i^{(0)}\rangle$ for some i. In this case, see Eq. (6.41),

$$c_n(0) = \delta_{ni}, \tag{6.48}$$

and therefore for all $m \neq i$ we have

$$c_m(t) = -\frac{\mathrm{i}\lambda}{\hbar} \int_0^t dt' P_{mi}(t') e^{\mathrm{i}\Omega_{mi}t'}. \tag{6.49}$$

The squared modulus $|\langle E_m^{(0)}|\Psi(t)\rangle|^2 = |c_m(t)|^2$ is the probability that a measurement of the energy yields the value $E_m^{(0)}$ or, equivalently, that the initial state $|E_i^{(0)}\rangle$ evolves to the state $|E_m^{(0)}\rangle$ at time t. This probability is correctly zero for $t = 0$, but it can become nonzero as t increases. In this case, we can say that the perturbation $\hat{P}(t)$ is responsible for inducing energy transitions from the initial level to another level. Note that for a transition to occur to a specific level m, the matrix element $P_{mi}(t)$ must be nonzero. For example, if $\hat{H}_0$ is the Hamiltonian of a one-dimensional harmonic oscillator and the initial state is the ground state of the harmonic oscillator, i.e., $|E_i^{(0)}\rangle = |0\rangle$, then a perturbation of the form $\hat{P}(t) = f(t)\hat{x}$ will never realize a transition to the levels $|m\rangle$ with $m > 1$ because $P_{mi}(t) = f(t)\langle m|\hat{x}|0\rangle = 0$ for all $m > 1$.

6.2.1 Fermi Golden Rule

An alternative and sometimes more convenient way to rewrite Eq. (6.49) is obtained in terms of the **Fourier transform** of the function $P_{mi}(t')$.

$$P_{mi}(t') = \int \frac{d\omega}{2\pi} e^{-\mathrm{i}\omega t'} \tilde{P}_{mi}(\omega). \tag{6.50}$$

Substituting into Eq. (6.49) and integrating with respect to time, we find

$$\begin{aligned} c_m(t) &= -\frac{\mathrm{i}\lambda}{\hbar} \int \frac{d\omega}{2\pi} \tilde{P}_{mi}(\omega) \int_0^t dt' e^{\mathrm{i}(\Omega_{mi}-\omega)t'} \\ &= -\frac{\mathrm{i}\lambda}{\hbar} \int \frac{d\omega}{2\pi} \tilde{P}_{mi}(\omega) e^{\mathrm{i}\frac{(\Omega_{mi}-\omega)t}{2}} \frac{\sin\left(\frac{\Omega_{mi}-\omega}{2}t\right)}{\left(\frac{\Omega_{mi}-\omega}{2}\right)}. \end{aligned} \tag{6.51}$$

Let us consider the special case of coherent and monochromatic perturbations, such as a laser. For these perturbations, the temporal dependence of the (Hermitian) operator $\hat{P}(t)$ is of the form

$$\hat{P}(t) = \hat{A}e^{\mathrm{i}\omega_0 t} + \hat{A}^\dagger e^{-\mathrm{i}\omega_0 t}, \tag{6.52}$$

where $\hat{A}$ can be any operator, even non-Hermitian, and ω_0 is the frequency of the laser used to perturb the system. Without loss of generality, we assume that $\omega_0 > 0$. From Eq. (6.45), we then have

$$P_{mi}(t) = A_{mi}e^{\mathrm{i}\omega_0 t} + A^*_{im}e^{-\mathrm{i}\omega_0 t}, \tag{6.53}$$

where we have defined the matrix elements of the operator $\hat{A}$ as $A_{mi} = \langle E^{(0)}_m|\hat{A}|E^{(0)}_i\rangle$. From Eq. (6.50), it is easy to obtain the Fourier transform

$$\tilde{P}_{mi}(\omega) = 2\pi A_{mi}\delta(\omega + \omega_0) + 2\pi A^*_{im}\delta(\omega - \omega_0). \tag{6.54}$$

The reader can easily verify that substituting this equation into Eq. (6.50) leads precisely to Eq. (6.53). Substituting Eq. (6.54) into Eq. (6.51), we find

$$c_m(t) = -\frac{\mathrm{i}\lambda}{\hbar}\left[A_{mi}e^{\mathrm{i}\frac{(\Omega_{mi}+\omega_0)t}{2}}\,\frac{\sin\left(\frac{\Omega_{mi}+\omega_0}{2}t\right)}{\left(\frac{\Omega_{mi}+\omega_0}{2}\right)} + A^*_{im}e^{\mathrm{i}\frac{(\Omega_{mi}-\omega_0)t}{2}}\,\frac{\sin\left(\frac{\Omega_{mi}-\omega_0}{2}t\right)}{\left(\frac{\Omega_{mi}-\omega_0}{2}\right)}\right]. \tag{6.55}$$

Let us study the coefficient $c_m(t)$ in the limit of long times. At a certain fixed time t, the function $\frac{\sin(\alpha t)}{\alpha}$ is an oscillating function with a frequency of t that tends to zero as $1/\alpha$. The absolute maximum occurs at $\alpha = 0$, where the function takes the value

$$\lim_{\alpha\to 0}\frac{\sin(\alpha t)}{\alpha} = t. \tag{6.56}$$

Therefore, in the limit $t \to \infty$, the dominating coefficients are those for which $\Omega_{mi} + \omega_0 = 0$ or $\Omega_{mi} - \omega_0 = 0$. This implies that in calculating $|c_m(t)|^2$, we can ignore the mixed terms as they are subdominant in the limit $t \to \infty$. In fact, if m is such that $\Omega_{mi} + \omega_0 = 0$, then the dominant contribution comes from the first term in the square bracket, while if m is such that $\Omega_{mi} - \omega_0 = 0$, then the dominant contribution comes from the second term in the square bracket. We can then write

$$\lim_{t\to\infty}|c_m(t)|^2 = \frac{\lambda^2}{\hbar^2}\lim_{t\to\infty}\left[|A_{mi}|^2\frac{\sin^2\left(\frac{\Omega_{mi}+\omega_0}{2}t\right)}{\left(\frac{\Omega_{mi}+\omega_0}{2}\right)^2} + |A_{im}|^2\frac{\sin^2\left(\frac{\Omega_{mi}-\omega_0}{2}t\right)}{\left(\frac{\Omega_{mi}-\omega_0}{2}\right)^2}\right] \tag{6.57}$$

To proceed, we need to study the function $g(\alpha, t) = \frac{\sin^2(\alpha t)}{\alpha^2}$. In Fig. 6.1, we show the behavior of the function for increasing values of t. It tends to zero as $1/\alpha^2$ for $\alpha \to \infty$ while it tends to the value t^2 for $\alpha \to 0$. Furthermore, as t increases, it

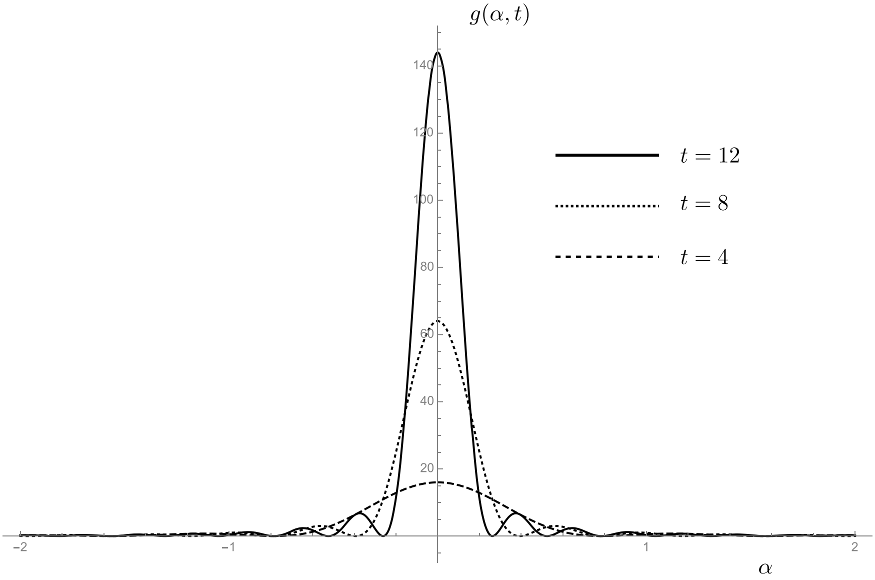

Fig. 6.1 Graph of the function $g(\alpha, t) = \frac{\sin^2(\alpha t)}{\alpha^2}$ with respect to α for various values of time t

becomes narrower since, descending from the main peak, it touches the α axis at the points $\pm\pi/t$. Therefore, we have a curve that, as t increases, is different from zero only near $\alpha = 0$ and for $\alpha = 0$ tends to infinity as t^2. This is the classic behavior of a Dirac delta function. We can then write

$$\lim_{t\to\infty} \frac{\sin^2(\alpha t)}{\alpha^2} = f(t)\delta(\alpha). \tag{6.58}$$

To determine the function $f(t)$, we integrate both sides of this equation with respect to α. Extending the integral to the complex plane and using the residue theorem, we obtain

$$f(t) = \int_{-\infty}^{\infty} d\alpha \frac{\sin^2(\alpha t)}{\alpha^2} = \pi t. \tag{6.59}$$

In light of these results, we can then write that

$$\lim_{t\to\infty} \frac{\sin^2\left(\frac{\Omega_{mi}\pm\omega_0}{2} t\right)}{\left(\frac{\Omega_{mi}\pm\omega_0}{2}\right)^2} = \pi t\, \delta\left(\frac{\Omega_{mi} \pm \omega_0}{2}\right) = 2\pi\hbar t\, \delta(E_m^{(0)} - E_i^{(0)} \pm \hbar\omega_0). \tag{6.60}$$

Substituting into Eq. (6.57), we arrive at the **Fermi golden rule**

$$\lim_{t\to\infty} \frac{|c_m(t)|^2}{t} = \lambda^2 \frac{2\pi}{\hbar} |A_{mi}|^2 \left[\delta(E_m^{(0)} - E_i^{(0)} + \hbar\omega_0) + \delta(E_m^{(0)} - E_i^{(0)} - \hbar\omega_0)\right]. \tag{6.61}$$

Therefore, the probability $|c_m(t)|^2$ that, starting from the initial state $|E_i^{(0)}\rangle$, the system evolves to the state $|E_m^{(0)}\rangle$ is different from zero only if $|A_{mi}|^2 \neq 0$ and at the same time, the energy difference between the initial and final states is $\pm\hbar\omega_0$. If the energy of the state $|E_m^{(0)}\rangle$ is greater than the energy of the initial state $|E_i^{(0)}\rangle$ (so only the second Dirac delta contributes), the transition process is called **absorption** because the energy increases and the system absorbs energy. Conversely, if the energy of the state $|E_m^{(0)}\rangle$ is less than the energy of the initial state $|E_i^{(0)}\rangle$ (so only the first Dirac delta contributes), the transition process is called **stimulated emission** because the energy decreases and the system emits energy.

The Fermi golden rule is of fundamental importance for the manipulation of quantum systems. For example, if we wanted to transition the electron initially in the ground state $|1, 0, 0\rangle$ of the hydrogen atom to a generic level $|n, l, m\rangle$, we would need to use an electromagnetic field with frequency $\omega_0 > 0$ such that $\hbar\omega_0 = E_n - E_1 = \frac{e^2}{2a_B}\left(1 - \frac{1}{n^2}\right)$ and ensure that the spatial part of the perturbation gives rise to a non-zero matrix element between the state $|1, 0, 0\rangle$ and the state $|n, l, m\rangle$.

6.2.2 *Radiation-Matter Interaction*

The electromagnetic fields are one of the most direct methods for transforming and manipulating quantum matter. They allow transforming an insulator into a metal, changing the color of a material, or transforming it from opaque to transparent and vice versa. In Sect. 4.4, we have seen that the Hamiltonian of a quantum particle in an electromagnetic field is given by Eq. (4.48). For low intensities, we can neglect the term proportional to A^2 and therefore rewrite Eq. (4.48) as

$$\hat{H} = \frac{\hat{p}^2}{2m} + Q\phi(\hat{\mathbf{r}}) - \frac{Q}{2mc}\Big(\hat{\mathbf{p}} \cdot \mathbf{A}(\hat{\mathbf{r}}, t) + \mathbf{A}(\hat{\mathbf{r}}, t) \cdot \hat{\mathbf{p}}\Big). \tag{6.62}$$

Comparing this Hamiltonian with Eq. (6.37), we see that

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + Q\phi(\hat{\mathbf{r}}), \tag{6.63}$$

$$\hat{P}(t) = \frac{Q}{2mc}\Big(\hat{\mathbf{p}} \cdot \mathbf{A}(\hat{\mathbf{r}}, t) + \mathbf{A}(\hat{\mathbf{r}}, t) \cdot \hat{\mathbf{p}}\Big). \tag{6.64}$$

This perturbation is known as the **radiation-matter interaction**.

If the electromagnetic field is monochromatic, then the vector potential has the form

$$\mathbf{A}(r, t) = \mathbf{A}_0 e^{-\mathrm{i}(\mathbf{k}\cdot\mathbf{r}-\omega_0 t)} + \mathbf{A}_0^* e^{\mathrm{i}(\mathbf{k}\cdot\mathbf{r}-\omega_0 t)} \tag{6.65}$$

where ω_0 is the frequency of the monochromatic field, and **k** is a vector with the direction of the field propagation and a magnitude of $|\mathbf{k}| = \omega_0/c$. For light with a frequency

$\omega_0 \leq \omega_{\text{XUV}}$, where $\omega_{\text{XUV}} \simeq 2\pi \times 3 \times 10^7$ GHz is the frequency of extreme ultraviolet, we have $|\mathbf{k}| < 2\pi \times 0.1\,\text{nm}^{-1}$. Therefore, for atoms and molecules, whose dimensions are at most a few nanometers, we can approximate the exponential $e^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \simeq 1$ for all frequencies below those of extreme ultraviolet. This approximation is called the **dipole approximation**. Considering that in a hydrogen atom, the ionization energy is 13.6 eV, see Eq. (4.189), we can reasonably expect that frequencies below ω_{XUV} allow observing electronic transitions in many atomic and molecular systems.

Comparing Eq. (6.65) with Eq. (6.52), we see that in the case of the radiation-matter interaction, the matrix element A_{mi} that appears in the Fermi golden rule is

$$A_{mi} = \frac{Q}{mc} \langle E_m^{(0)} | \hat{\mathbf{p}} \cdot \mathbf{A}_0 | E_i^{(0)} \rangle. \tag{6.66}$$

6.3 Variational Method

Consider a time-independent Hamiltonian $\hat{H}$. The **variational method** is a *non-perturbative* approach aimed at obtaining an approximation for the ground state of $\hat{H}$, let us call it $|\Psi_0\rangle$, and its energy E_0. It is based on the following simple consideration. For any normalized ket $|\Psi\rangle$, the **variational principle** holds:

$$\langle \Psi | \hat{H} | \Psi \rangle \geq E_0. \tag{6.67}$$

The proof of the inequality (6.67) is immediate. We denote by $|\Psi_n\rangle$ and E_n the eigenkets and eigenvalues of $\hat{H}$. Among these, there is obviously the ground state $|\Psi_0\rangle$ with energy E_0, and by definition $E_n \geq E_0$. The kets $|\Psi_n\rangle$ form an orthonormal basis on which we can expand $|\Psi\rangle$:

$$|\Psi\rangle = \sum_n c_n |\Psi_n\rangle, \qquad \sum_n |c_n|^2 = 1, \tag{6.68}$$

where the second equation expresses the normalization condition $\langle \Psi | \Psi \rangle = 1$. It follows that

$$\langle \Psi | \hat{H} | \Psi \rangle = \sum_n |c_n|^2 E_n \geq E_0 \sum_n |c_n|^2 = E_0. \tag{6.69}$$

The variational principle expresses the fact that the mean value of the Hamiltonian operator on any normalized ket is always greater than (or at most equal to) the energy of the ground state.

Let us now see how to use the variational principle to formulate the variational method. Suppose you have a certain physical intuition about the structure of the ground state. Consider, for example, a particle in one dimension subjected to the potential $V(x)$ shown in Fig. 6.2. If this potential admits a ground state with negative energy, it would be a bound state, and the corresponding wavefunction would be

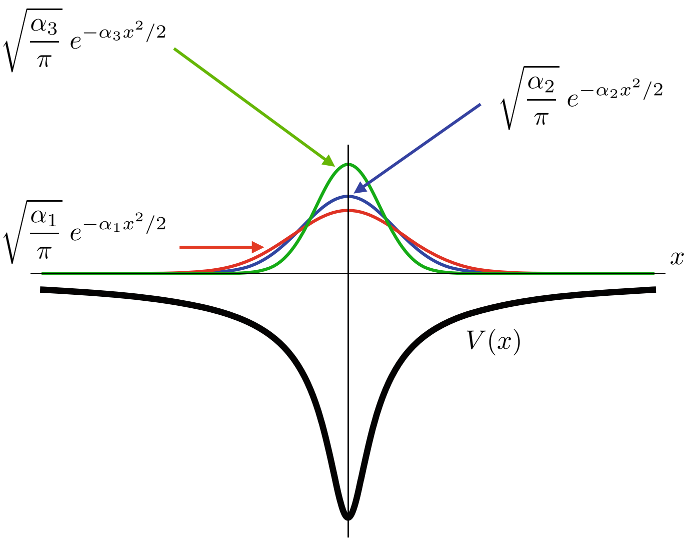

Fig. 6.2 Example of variational functions for the approximate calculation of the ground state of a particle subjected to the potential $V(x)$

maximum at the minimum of the potential, approaching zero far from the minimum. We could then approximate the ground state with a normalized Gaussian function

$$\Psi_\alpha(x) = \langle x|\Psi_\alpha\rangle = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}, \tag{6.70}$$

and, correspondingly, obtain an approximation to the energy of the ground state by calculating the mean value $E(\alpha) = \langle\Psi_\alpha|\hat{H}|\Psi_\alpha\rangle$. But which value to choose for the parameter α? In Fig. 6.2, we show three different functions $\Psi_\alpha(x)$ corresponding to three different values of α. The inequality (6.67) implies that $E(\alpha)$ is greater than E_0 for all α. The best choice of α, i.e., the one for which $E(\alpha)$ is closest to E_0, corresponds to the value for which $E(\alpha)$ is minimized. This leads us to compute the best value of α by solving the stationarity equation

$$\frac{dE(\alpha)}{d\alpha} = 0; \tag{6.71}$$

among all possible solutions of this equation, we select the one corresponding to the absolute minimum of $E(\alpha)$.

More generally, the variational method consists of writing a "variational" ket $|\Psi_{\alpha,\beta,\gamma,\ldots}\rangle$, depending on parameters α, β, γ, ..., which we expect can well approximate the ground state for a certain choice of parameters. Since the mean value

$$E(\alpha, \beta, \gamma, \ldots) = \langle\Psi_{\alpha,\beta,\gamma,\ldots}|\hat{H}|\Psi_{\alpha,\beta,\gamma,\ldots}\rangle \geq E_0, \tag{6.72}$$

the best choice of parameters corresponds to the values at which the function $E(\alpha, \beta, \gamma, \ldots)$ is minimized.

6.4 Exercises

1. Consider a one-dimensional quantum harmonic oscillator of frequency ω and let $|n\rangle$, with $n = 0, 1, 2, \ldots$, be the eigenstates of energy $E_n = \hbar\omega(n + 1/2)$. The Hamiltonian can therefore be written as $\hat{H} = \sum_{n \geq 0} E_n |n\rangle\langle n|$. Let a small perturbation be given by

$$\hat{P} = \lambda\hbar\omega \sum_{n>0} \sqrt{nv^n}(|n\rangle\langle 0| + |0\rangle\langle n|)$$

with $\lambda \ll 1$ and v a numerical constant greater than zero. Determine the ground state energy correction to the first and second order in λ. Is the correction finite regardless of the value of v? If not, determine for which value of v the correction diverges.

Solution *To first order we have* $E_0^{(1)} = \langle 0|\hat{P}|0\rangle = 0$. *To second order we have* $E_0^{(2)} = -\sum_{n>0} |\langle 0|\hat{P}|n\rangle|^2/(n\hbar\omega)$. *Since* $\langle 0|\hat{P}|n\rangle = \lambda\hbar\omega\sqrt{nv^n}$ *we have*

$$E_0^{(2)} = -\sum_{n>0} \frac{(\lambda\hbar\omega)^2 nv^n}{n\hbar\omega} = -\lambda^2\hbar\omega \sum_{n>0} v^n \tag{6.73}$$

So $E_0^{(2)}$ *is finite only for* $v < 1$ *and holds* $E_0^{(2)} = -\lambda^2\hbar\omega\frac{v}{1-v}$

2. A three-level quantum system is described by the Hamiltonian

$$\mathbb{H} = \begin{pmatrix} 3/2 & 0 & \mathrm{i}/2 \\ 0 & 1 & 0 \\ -\mathrm{i}/2 & 0 & 3/2 \end{pmatrix}$$

i. Find the eigenvalues, their degeneracy, and an orthonormal basis of eigenvectors

ii. The system is then subject to the perturbation $\mathbb{P} = \lambda \begin{pmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$. Calculate the eigenvalue correction to first order in λ and an orthonormal basis of eigenvectors to order zero in λ.

Solution *i. The Hamiltonian* $\mathbb{H}$ *has eigenvalues* $E_1 = 1$ *with eigenvector* $\phi_1 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$, $E_2 = 1$ *with eigenvector* $\phi_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} -\mathrm{i} \\ 0 \\ 1 \end{pmatrix}$ *and* $E_3 = 2$ *with eigenvector* $\phi_3 = \frac{1}{\sqrt{2}} \begin{pmatrix} \mathrm{i} \\ 0 \\ 1 \end{pmatrix}$.

ii. Since $E_1 = E_2 = 1$ *we must apply the perturbation theory for degenerate states. In the degenerate subspace we have*

$$\begin{pmatrix} \phi_1^\dagger \mathbb{P} \phi_1 & \phi_1^\dagger \mathbb{P} \phi_2 \\ \phi_2^\dagger \mathbb{P} \phi_1 & \phi_2^\dagger \mathbb{P} \phi_2 \end{pmatrix} = \lambda \begin{pmatrix} 1 & \mathrm{i}/\sqrt{2} \\ -\mathrm{i}/\sqrt{2} & 1/2 \end{pmatrix}$$

which provides the corrections $E_1^{(1)} = 0$, *with new eigenvector* $\psi_1 = -\frac{\mathrm{i}}{\sqrt{3}}\phi_1 + \sqrt{\frac{2}{3}}\phi_2$, *and* $E_2^{(1)} = 3\lambda/2$, *with new eigenvector* $\psi_2 = \mathrm{i}\sqrt{\frac{2}{3}}\phi_1 + \frac{1}{\sqrt{3}}\phi_2$. *The eigenvalue* E_3 *is non-degenerate and therefore the correction is simply* $E_3^{(1)} = \phi_3^\dagger \mathbb{P} \phi_3 = \lambda/2$ *with unchanged eigenvector* ϕ_3.

3. Consider the Hamiltonian in three dimensions for an electron immersed in the central potential generated by a positive point-like charge Ze: $\hat{H} = \frac{\hat{p}^2}{2m} - \frac{Ze^2}{\hat{r}}$. Consider the small perturbation $\hat{P} = \lambda\delta(\hat{r} - d)$ with $d \geq 0$.
i. Calculate the correction to the energy of the first excited state to first order in λ.
ii. For what values of d is the degeneracy not removed?
Solution *i. Having the potential a spherical symmetry and being the spherical harmonics mutually orthogonal the matrix* 4×4 *which represents the perturbation in the basis of the degenerate eigenstates is diagonal. So the corrections to the energies are simply given by*

$$\delta E_0 = \int dr\, r^2 V(r) \int d\Omega\, |\Psi_{200}(r, \theta, \varphi)|^2 = \lambda \left(\frac{1}{2a_0}\right)^3 d^2 \left(2 - \frac{d}{a_0}\right)^2 e^{-\frac{d}{a_0}}$$

$$\delta E_1 = \int dr\, r^2 V(r) \int d\Omega\, |\Psi_{21m}(r, \theta, \varphi)|^2 = \lambda \left(\frac{1}{2a_0}\right)^3 d^2 \left(\frac{d}{\sqrt{3}a_0}\right)^2 e^{-\frac{d}{a_0}}$$

The degeneracy is only partially removed since δE_1 *does not depend on* m
ii. For the degeneracy to remain four it must hold $\delta E_0 = \delta E_1$. *This happens for* $d = 0$ *and for* $d = \frac{2}{1 \pm \frac{1}{\sqrt{3}}} a_0$.

4. Let $|n\rangle$ and $\langle n|$ be the auto-kets and the auto-bra of the Hamiltonian of the one-dimensional harmonic oscillator with eigenvalues $\varepsilon_n = \hbar\omega(n + \frac{1}{2})$, and consider the Hamiltonian $\hat{H} = \sum_{n=0}^{\infty} \varepsilon_n |n\rangle\langle n| + \sqrt{2}\hbar\omega(|0\rangle\langle 1| + |1\rangle\langle 0|)$.
i. Determine the eigenstates of $\hat{H}$ and their respective energies;

ii. If the system is subject to the perturbation $\hat{P} = \hbar\eta(|0\rangle\langle 2| + |2\rangle\langle 0|)$ with $\eta \ll \omega$, determine how the energies change to first order in perturbation theory.

Solution *i.* $\hat{H}$ *can be rewritten as* $\hat{H} = \sum_{n=2}^{\infty} \varepsilon_n |n\rangle\langle n| + \frac{\hbar\omega}{2}|0\rangle\langle 0| + \frac{3\hbar\omega}{2}|1\rangle\langle 1| + \sqrt{2}\hbar\omega(|0\rangle\langle 1| + |1\rangle\langle 0|)$. *Therefore it is evident that the kets* $|n\rangle$ *with* $n \geq 2$ *are eigenkets of* $\hat{H}$ *with eigenvalues* ε_n, *equal to those of the normal harmonic oscillator. Instead the kets* $|0\rangle$ *and* $|1\rangle$ *are no longer autokets as they are mixed by the perturbation. In the subspace generated by the basis* $\{|0\rangle, |1\rangle\}$ *the Hamiltonian is represented by the* 2×2 *matrix*

$$\hbar\omega \begin{pmatrix} \frac{1}{2} & \sqrt{2} \\ \sqrt{2} & \frac{3}{2} \end{pmatrix}$$

whose eigenvalues are $\varepsilon_- = -\frac{\hbar\omega}{2}$ *(which being the lowest is the ground state energy) and* $\varepsilon_+ = \frac{5\hbar\omega}{2}$. *We note that the eigenvalue* $\frac{5\hbar\omega}{2}$ *is two times degenerate, since* $\varepsilon_+ = \varepsilon_2$. *The respective normalized eigenvectors are instead*

$$\varphi_- = \frac{1}{\sqrt{3}}\begin{pmatrix} 1 \\ \sqrt{2} \end{pmatrix} \quad \text{e} \quad \varphi_+ = \frac{1}{\sqrt{3}}\begin{pmatrix} -\sqrt{2} \\ 1 \end{pmatrix}.$$

So the autokets are $|\varphi_-\rangle = \frac{1}{\sqrt{3}}(|0\rangle + \sqrt{2}|1\rangle)$ e $|\varphi_+\rangle = \frac{1}{\sqrt{3}}(-\sqrt{2}|0\rangle + |1\rangle)$.
ii. On all non-degenerate states the perturbation has no effect to first order, since $\langle n|\hat{P}|n\rangle = \langle\varphi_-|\hat{P}|\varphi_-\rangle = 0$. *On the two degenerate states* $|\varphi_+\rangle$ *and* $|2\rangle$ *the matrix elements of* $\hat{P}$ *instead are not zero:*

$$\begin{pmatrix} \langle\varphi_+|\hat{P}|\varphi_+\rangle & \langle\varphi_+|\hat{P}|2\rangle \\ \langle 2|\hat{P}|\varphi_+\rangle & \langle 2|\hat{P}|2\rangle \end{pmatrix} = \hbar\eta \begin{pmatrix} 0 & -\sqrt{\frac{2}{3}} \\ -\sqrt{\frac{2}{3}} & 0 \end{pmatrix}$$

The eigenvalues of this matrix are $\pm\sqrt{\frac{2}{3}}\hbar\eta$. *Therefore the perturbation removes the degeneracy and the corrected energies to first order are* $\frac{5}{2}\hbar\omega - \sqrt{\frac{2}{3}}\hbar\eta$ *and* $\frac{5}{2}\hbar\omega + \sqrt{\frac{2}{3}}\hbar\eta$.

5. Consider a particle of mass m in one dimension described by the Hamiltonian $\hat{H}_0 = \frac{\hat{p}^2}{2m} + V(\hat{x})$ where

$$V(x) = \begin{cases} 0 & 0 < x < L \\ \infty & \text{otherwise} \end{cases}$$

The particle is initially in the ground state of $\hat{H}_0$ and is then disturbed by the time-dependent perturbation

$$\lambda\hat{P}(t) = \lambda\frac{\hbar L}{2}\delta\left(\hat{x} - \frac{L}{2}\right)\delta\left(t - \frac{4mL^2}{\pi\hbar}\right)$$

Calculate to the lowest order in λ the probability of measuring energy $E_n^{(0)} = \frac{\hbar^2\pi^2 n^2}{2mL^2}$ at a generic time t.

Solution *We denote by* $|E_n^{(0)}\rangle$ *the eigenkets of* $\hat{H}_0$ *and by* $\varphi_n(x) = \langle x|E_n^{(0)}\rangle = \sqrt{\frac{2}{L}}\sin(\frac{n\pi x}{L})$ *the corresponding eigenfunctions. From the time-dependent perturbation theory the the required probability is given by* $|c_n(t)|^2$ *where*

$$\begin{aligned}
c_n(t) &= -\mathrm{i}\frac{\lambda}{\hbar}\int_0^t dt'\langle E_n^{(0)}|\hat{P}(t')|E_1^{(0)}\rangle\, e^{\mathrm{i}(E_n^{(0)}-E_1^{(0)})t'/\hbar} \\
&= -\mathrm{i}\frac{\lambda}{\hbar}\frac{\hbar L}{2}\int_0^t dt'\int dx\langle E_n^{(0)}|x\rangle\langle x|\delta\left(\hat{x} - \frac{L}{2}\right)|E_1^{(0)}\rangle\delta\left(t' - \frac{4mL^2}{\pi\hbar}\right)e^{\mathrm{i}(E_n^{(0)}-E_1^{(0)})t'/\hbar} \\
&= -\mathrm{i}\frac{\lambda L}{2}\int_0^t dt'\delta\left(t' - \frac{4mL^2}{\pi\hbar}\right)e^{\mathrm{i}(E_n^{(0)}-E_1^{(0)})t'/\hbar}\int dx\ \varphi_n(x)\varphi_1(x)\delta\left(x - \frac{L}{2}\right)
\end{aligned}$$

So the probability is zero if $t < \frac{4mL^2}{\pi\hbar}$. *Instead, in the case where* $t > \frac{4mL^2}{\pi\hbar}$ *we have*

$$c_n(t) = -\mathrm{i}\lambda\sin\frac{n\pi}{2}e^{\mathrm{i}\frac{\hbar^2\pi^2}{2mL^2}(n^2-1)\frac{4mL^2}{\pi\hbar^2}} = -\mathrm{i}\lambda\sin\frac{n\pi}{2}$$

6. Consider a quantum system describable by a basis of only three orthonormal kets $|1\rangle$, $|2\rangle$ and $|3\rangle$. In this basis the Hamiltonian operator is given by $\hat{H}_0 = E_0\sum_{n=1}^{3} n\ |n\rangle\langle n| + \sqrt{2}E_0\ (|2\rangle\langle 3| + |3\rangle\langle 2|)$. The system is in the state $|\psi\rangle = \frac{1}{\sqrt{3}}(\,|1\rangle + \mathrm{i}|2\rangle + |3\rangle\,)$.
i. Find the possible values of energy and calculate the probabilities of measuring them.
ii. Calculate to first order in λ how the energies of $\hat{H}_0$ are corrected if the Hamiltonian becomes $\hat{H}_0 + \lambda\hat{P}$ with $\hat{P} = \mathrm{i}(|1\rangle\langle 3| - |3\rangle\langle 1|)$. Using the eigenkets of $\hat{H}_0 + \lambda\hat{P}$ to zero order in λ compute the probabilities of measuring the correct energies.

Solution *In the given basis the Hamiltonian is represented by the matrix*

$$\mathbb{H} = E_0\begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & \sqrt{2} \\ 0 & \sqrt{2} & 3 \end{pmatrix}$$

This matrix admits eigenvalue E_0 *with degeneracy 2 e eigenvalue* $4E_0$ *with degeneracy 1. The two orthonormals eigenkets with eigenvalue* E_0 are $|\phi_1^{(a)}\rangle =$

$|1\rangle$ and $|\phi_1^{(b)}\rangle = \frac{1}{\sqrt{3}}(\sqrt{2}|2\rangle - |3\rangle)$ while the eigenvector with eigenvalue $4E_0$ is $|\phi_4\rangle = \frac{1}{\sqrt{3}}(|2\rangle + \sqrt{2}|3\rangle)$.

i. The probability of measuring E_0 is given by

$$P(E_0) = |\langle\psi|\phi_1^{(a)}\rangle|^2 + |\langle\psi|\phi_1^{(b)}\rangle|^2 = \frac{1}{3} + \frac{1}{9}|-i\sqrt{2}-1|^2 = \frac{2}{3}$$

and therefore that of measuring $4E_0$ is $P(4E_0) = 1 - P(E_0) = \frac{1}{3}$.

ii. To calculate the corrections we use the perturbation theory. In the case of the degenerate eigenvalue we have to construct the matrix

$$\mathbb{P} = \begin{pmatrix} \langle\phi_1^{(a)}|\hat{P}|\phi_1^{(a)}\rangle & \langle\phi_1^{(a)}|\hat{P}|\phi_1^{(b)}\rangle \\ \langle\phi_1^{(b)}|\hat{P}|\phi_1^{(a)}\rangle & \langle\phi_1^{(b)}|\hat{P}|\phi_1^{(b)}\rangle \end{pmatrix} = \frac{1}{\sqrt{3}}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}$$

Then the degenerate eigenvalue splits into two distinct eigenvalues equal to $E_0 + \lambda/\sqrt{3}$ and $E_0 - \lambda/\sqrt{3}$; the zeroth-order eigenkets in λ are respectively $|\phi_1^{(+)}\rangle = \frac{1}{\sqrt{2}}(|\phi_1^{(a)}\rangle + \mathrm{i}|\phi_1^{(b)}\rangle)$ and $|\phi_1^{(-)}\rangle = \frac{1}{\sqrt{2}}(|\phi_1^{(a)}\rangle - \mathrm{i}|\phi_1^{(b)}\rangle)$. In the case of the non-degenerate eigenvalue it is enough to calculate $\langle\phi_4|\hat{P}|\phi_4\rangle = 0$; therefore the perturbation does not give rise a correction and the eigenket does not change to zero order in λ. Once we know the zeroth-order corrected eigenkets we can easily calculate the required probabilities. We have $P(E_0 + \lambda/\sqrt{3}) = |\langle\psi|\phi_1^{(+)}\rangle|^2 = \frac{1}{3}(1 + \sqrt{\frac{2}{3}})$. Using that the probability of the eigenvalue $4E_0$ does not change we have $P(E_0 - \lambda/\sqrt{3}) = 1 - P(E_0 + \lambda/\sqrt{3}) - P(4E_0) = \frac{1}{3}(1 - \sqrt{\frac{2}{3}})$.

7. Consider the electron in a Hydrogen atom subject to perturbation

$$\hat{P} = \lambda \frac{\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}}{\hat{r}^4}$$

where $\hat{\mathbf{L}} = (\hat{L}_x, \hat{L}_y, \hat{L}_z)$ is the vector of angular momentum operators, $\hat{\mathbf{S}} = (\hat{S}_x, \hat{S}_y, \hat{S}_z)$ is the vector of spin operators and $\hat{r}$ is the operator for the radial coordinate. Determine the first order corrections in λ to the energy of the first excited state.

Solution *The degenerate kets are $|2, 0, 0\rangle|s, m_s\rangle$ and $|2, 1, m\rangle|s, m_s\rangle$ where $s = 1/2$, $m_s = \pm 1/2$ is the spin of the electron and $m = -1, 0, 1$ is the quantum azimuthal number. The level degeneracy is therefore equal to 8. We rewrite the perturbation as*

$$\hat{P} = \frac{\lambda}{2} \frac{\hat{J}^2 - \hat{L}^2 - \hat{S}^2}{\hat{r}^4}$$

where $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$ is the total angular momentum. So the perturbation is diagonal in the basis of total angular momentum. The kets $|2, 0, 0\rangle|m_s\rangle = |2, j, m_j\rangle_{0s}$

are eigenkets of $\hat{P}$ *with zero eigenvalue, hence their energy is not corrected. Starting from the kets* $|2, 1, 0\rangle|s, m_s\rangle$ *we can construct the kets* $|2, j, m_j\rangle_{1s}$ *with* $j = 1/2, 3/2$. *It turns out*

$$
\begin{aligned}
{}_{1s}\langle 2, j, m_j|\hat{P}|2, j, m_j\rangle_{1s} &= \frac{\lambda\hbar^2}{2}\left[j(j+1) - 11/4\right] \int\limits_0^\infty dr \frac{r^2|R_{2,1}(r)|^2}{r^4} \\
&= \frac{\lambda\hbar^2}{48a_\mathrm{B}^4}\left[j(j+1) - 11/4\right]
\end{aligned}
$$

Therefore we have a correction equal to $-\frac{\lambda\hbar^2}{24a_\mathrm{B}^4}$ *with degeneracy 2 (corresponding to* $j = 1/20$*) and a correction equal to* $\frac{\lambda\hbar^2}{48a_\mathrm{B}^4}$ *with degeneracy 4 (corresponding to* $j = 3/2$*).*

8. Consider an electron in the ground state of a Hydrogen atom. Between the time $t = 0$ and the time $t = T$ a perturbation depending on time and on the radial coordinate is switched on

$$
\lambda P(r, t) = \lambda\, \frac{\sqrt{2}\,\hbar\, a_\mathrm{B}}{T}\, \exp\left[\left(\frac{3}{2}v - i\frac{3e^2}{8\hbar}\right)\frac{t}{a_\mathrm{B}}\right]\delta(r - vt)
$$

where a_B is the Bohr radius and $v > 0$ is a constant with physical dimensions of a velocity. Neglecting the spin degrees of freedom calculate to lowest order in λ the probabilities at time $t = T$ to find the electron in one of the eigenstates with principal quantum number $n = 2$. For which value of v is this probability minimal?

Solution *Since the perturbation does not depend on the angular variables the probability of finding the electron in states with* $n = 2$ *and angular momentum* $l = 1$ *is zero (orthonormality of spherical harmonics). To know the probability of finding the electron with* $n = 2$ *and* $l = 0$ *we need to calculate*

$$
\begin{aligned}
c_{2,0} &= -\frac{\mathrm{i}\lambda}{\hbar}\int\limits_0^T dt' \int\limits_0^\infty dr\, r^2 R_{1,0}(r) R_{2,0}(r) P(r, t') e^{\mathrm{i}(E_2 - E_1)t'/\hbar} \\
&= -\frac{\mathrm{i}\lambda}{\hbar}\, 2\left(\frac{1}{a_\mathrm{B}}\right)^{3/2}\left(\frac{1}{2a_\mathrm{B}}\right)^{3/2}\frac{\sqrt{2}\,\hbar\, a_\mathrm{B}}{T} \\
&\quad\times \int\limits_0^T dt' \int\limits_0^\infty dr\, r^2 e^{-\frac{3}{2}\frac{r}{a_\mathrm{B}}}\left(2 - \frac{r}{a_\mathrm{B}}\right) e^{\left(\frac{3}{2}v - \mathrm{i}\frac{3e^2}{8\hbar}\right)\frac{t'}{a_\mathrm{B}}}\, e^{\mathrm{i}\frac{3e^2 t'}{8a_\mathrm{B}\hbar}}\, \delta(r - vt') \\
&= -\mathrm{i}\frac{\lambda}{a_\mathrm{B}^2 T}\int\limits_0^T dt' (vt')^2\left(2 - \frac{vt'}{a_\mathrm{B}}\right) \\
&= -\mathrm{i}\lambda\left(\frac{vT}{a_\mathrm{B}}\right)^2\left(\frac{2}{3} - \frac{vT}{4a_\mathrm{B}}\right)
\end{aligned}
\tag{6.74}
$$

The required probability is $P_{2,0} = |c_{2,0}|^2 = \lambda^2 \left(\frac{vT}{a_B}\right)^4 \left(\frac{2}{3} - \frac{vT}{4a_B}\right)^2$. *The minimum value is zero and we have it for* $v = \frac{8a_B}{3T}$.

9. Consider a particle of mass m on a sphere of radius R having Hamiltonian

$$\hat{H} = \frac{\hat{L}_x^2 + \hat{L}_y^2}{2mR^2}$$

Knowing that the a measure of the operator $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ provides always the value $2\hbar^2$

i. What is the lowest value that a measure of energy can provide

ii. What are the eigenstates corresponding to this lowest value?

iii. How is this lowest value corrected if you turn on the perturbation $P(\theta, \phi) = \lambda\delta(\phi - \theta)$?

Solution *i. We rewrite the Hamiltonian as* $\hat{H} = \frac{\hat{L}^2 - \hat{L}_z^2}{2mR^2}$. *Since* $\hat{L}^2$ *gives with certainty* $2\hbar^2$ *it must be* $l = 1$ *and so the possible values of* $\hat{L}_z$ *are* $\hbar m$ *with* $m = -1, 0, 1$. *Using the fact that* $\hat{L}^2$ *and* $\hat{L}_z$*commute the possible values of the energy are* $\frac{\hbar^2}{2mR^2}(2 - m^2)$. *So the lowest eigenvalue is* $\frac{\hbar^2}{2mR^2}$.
ii. The eigenstates corresponding to the lowest eigenvalue are $|1, 1\rangle$ *and* $|1, -1\rangle$.
iii. The perturbation corrects the lowest eigenvalue. To calculate the correction it is necessary to preliminarily determine the matrix of elements

$$P_{m,m'} = \lambda \int d\Omega\, Y_{1,m}^*(\theta, \phi)\delta(\phi - \theta)Y_{1,m'}(\theta, \phi) = \lambda \int_0^\pi d\theta \sin\theta\, Y_{1,m}^*(\theta, \theta)Y_{1,m'}(\theta, \theta).$$

We have

$$P_{1,1} = P_{-1,-1} = \lambda\frac{3}{8\pi}\int_0^\pi d\theta(\sin\theta)^3 = \lambda\frac{3}{8\pi}\int_{-1}^1 dx(1 - x^2) = \frac{\lambda}{2\pi}$$

$$P_{1,-1} = P_{-1,1} = \lambda\frac{3}{8\pi}\int_0^\pi d\theta(\sin\theta)^3 e^{-2i\theta} = \lambda\frac{3}{8\pi}\int_0^\pi d\theta(\sin\theta)^3(\cos(2\theta) - \mathrm{i}\sin(2\theta))$$

In this last integral the imaginary part is zero since $\sin(2\theta) = 2\sin\theta\cos\theta$ *and* $\int_0^\pi d\theta(\sin\theta)^4\cos\theta = 0$. *As for the real part we use that* $\cos(2\theta) = 2(\cos\theta)^2 - 1$. *So* $P_{1,-1} = P_{-1,1} = \lambda\frac{3}{8\pi}\int_{-1}^1 dx(1 - x^2)(2x^2 - 1) = -\frac{3\lambda}{10\pi}$ *The energy corrections are then given by the eigenvalues of the matrix*

$$P = \frac{\lambda}{2\pi}\begin{pmatrix} 1 & -3/5 \\ -3/5 & 1 \end{pmatrix}.$$

It is immediate to verify that the eigenvalues are given by $\frac{\lambda}{2\pi}(1 \pm \frac{3}{5})$.

10. A Hydrogen atom initially in its ground state is illuminated by a weak electromagnetic radiation of frequency $\omega > 0$ and polarized along the z axis, described by the operator $\hat{P}(t)$, with $\hat{P}(t) = \hat{z} E_0 \sin(\omega t)$. Neglecting the spin-orbit interaction, calculate to lowest order in E_0 the probability of transition per unit of time to the first excited state in the limit $t \to \infty$, as ω varies.

    Remember that, see Appendix C, $\int_0^\infty dx\, x^n e^{-x} = n!$.

    Solution *The first excited state has* 4 *degeneracy, with eigenfunctions* $\Psi_{200} = R_{20} Y_{00}$, $\Psi_{211} = R_{21} Y_{11}$, $\Psi_{210} = R_{21} Y_{10}$ *and* $\Psi_{21-1} = R_{21} Y_{1-1}$. *It is therefore necessary to calculate 4 probabilities e then add them. According to Fermi's golden rule these probabilities in the long time limit are given by*

$$\begin{aligned}\frac{P_{nlm}}{t} &= E_0^2 \frac{2\pi}{\hbar} \left| \langle \Psi_{100} | \hat{z} | \Psi_{nlm} \rangle \right|^2 \delta(E_2 - E_1 - \hbar\omega_0) \\ &= E_0^2 \frac{2\pi}{\hbar} \left| \int_0^\infty dr r^3 R_{10} R_{nl} \int_0^\pi d\theta \int_0^{2\pi} d\phi \, \sin\theta \cos\theta Y_{00} Y_{lm} \right|^2 \delta(E_2 - E_1 - \hbar\omega_0)\end{aligned}$$

where we write $z = r\cos\theta$. *It's easy to verify that* $P_{211} = P_{21-1} = 0$ *since* $\int_0^{2\pi} d\phi \, e^{\pm i\phi} = 0$. *We also have* $P_{200} = 0$ *since* $\int_0^\pi \delta\theta \, \sin\theta \cos\theta = 0$. *The only non-zero probability is therefore* P_{210}. *It turns out*

$$\begin{aligned}\int_0^\pi d\theta \int_0^{2\pi} d\phi \sin\theta \cos\theta \frac{1}{\sqrt{4\pi}} \sqrt{\frac{3}{4\pi}} \cos\theta &= \frac{2\pi\sqrt{3}}{4\pi} \int_{-1}^{1} d(\cos\theta) \, \cos^2\theta \\ &= \frac{2\pi\sqrt{3}}{4\pi} \frac{2}{3} = \frac{1}{\sqrt{3}}\end{aligned}$$

and

$$\begin{aligned}\int_0^\infty dr r^3 \, 2 \left(\frac{1}{a_B}\right)^{3/2} e^{-\frac{r}{a_B}} \left(\frac{1}{2a_B}\right)^{3/2} e^{-\frac{r}{2a_B}} \frac{r}{\sqrt{3}\, a_B} &= \frac{1}{\sqrt{6}} \frac{1}{a_B^4} \int_0^\infty dr r^4 e^{-\frac{3r}{2a_B}} \\ &= \frac{1}{\sqrt{6}} \frac{1}{a_B^4} \left(\frac{2a_B}{3}\right)^5 \int_0^\infty dx x^4 e^{-x} \\ &= \frac{1}{\sqrt{6}} \frac{1}{a_B^4} \left(\frac{2a_B}{3}\right)^5 4! = a_B \frac{2^8}{3^4\sqrt{6}}\end{aligned}$$

Therefore the probability per unit time to measure energy E_2 is equal to

$$\frac{P(E_2)}{t} = E_0^2 \frac{2\pi}{\hbar} a_B^2 \frac{2^{15}}{3^{10}} \delta(E_2 - E_1 - \hbar\omega_0)$$

11. Consider a spin 1/2 electron described by the Hamiltonian of the Hydrogen atom $\hat{H} = \frac{\hat{p}^2}{2m} - \frac{e^2}{\hat{r}}$. The energy eigenkets are therefore the kets $|n, l, m\rangle|\pm\rangle$, where $|\pm\rangle$ are the two projections of the spin, and have energy $E_n = -e^2/(2n^2 a_\mathrm{B})$. The electron is initially in the state

$$|\Psi\rangle = |1, 0, 0\rangle|+\rangle.$$

At time $t = 0$ the perturbation is turned on

$$\hat{P}(t) = \frac{9a_\mathrm{B}\eta}{\hbar}\, e^{-\eta t}\, \frac{\hat{J}^2}{\hat{r}}$$

where $\eta = (E_2 - E_1)/\hbar > 0$ and $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$ is the total angular momentum. The probability is asked for the lowest order in perturbation theory that at time t, the electron can be found in the states $|2, 1, 0\rangle|+\rangle$ e $|2, 0, 0\rangle|+\rangle$.

Solution *We have* $\hat{P}(t)|\Psi\rangle = \lambda\frac{3\hbar^2}{4}\frac{e^{-\eta t}}{\hat{r}}|1, 0, 0\rangle|+\rangle$. *As the spherical harmonics are orthogonal the probability of transition into the state* $|2, 1, 0\rangle|+\rangle$ *is zero. To calculate the probability of transition into the state* $|2, 0, 0\rangle|+\rangle$ *we must calculate the coefficient*

$$\begin{aligned} c(t) &= -\frac{\mathrm{i}}{\hbar}\int_0^t dt' \langle +|\langle 2, 0, 0|\hat{P}(t)|1, 0, 0\rangle|+\rangle\, e^{\mathrm{i}\eta t'} \\ &= -\mathrm{i}\frac{27a_\mathrm{B}\eta}{4}\int_0^t dt' e^{(\mathrm{i}-1)\eta t'}\int_0^\infty dr\, r\, R_{2,0}(r)R_{1,0}(r) \end{aligned}$$

The radial integral provides

$$\begin{aligned} \int_0^\infty dr\, r\, R_{2,0}(r)R_{1,0}(r) &= \frac{1}{\sqrt{2}}\frac{1}{a_\mathrm{B}^3}\left[2\left(\frac{2a_\mathrm{B}}{3}\right)^2\int_0^\infty dx\, xe^{-x} - \frac{1}{a_\mathrm{B}}\left(\frac{2a_\mathrm{B}}{3}\right)^3\int_0^\infty dx\, x^2e^{-x}\right] \\ &= -\frac{8}{27\sqrt{2}\, a_\mathrm{B}} \end{aligned}$$

The time integral provides

$$\int_0^t dt' e^{(i-1)\eta t'} = \frac{e^{(i-1)\eta t} - 1}{(i-1)\eta}$$

So the required probability is

$$P(t) = |c(t)|^2 = \left(\frac{27a_{\mathrm{B}}\eta}{4}\right)^2 \times \frac{64}{2(27)^2a_{\mathrm{B}}^2}\frac{|e^{(i-1)\eta t}-1|^2}{2\eta^2} = 1 + e^{-2\eta t} - 2e^{-\eta t}\cos(\eta t)$$

12. Consider a spinless particle described by the Hamiltonian of the Hydrogen atom $\hat{H} = \frac{\hat{p}^2}{2m} - \frac{e^2}{\hat{r}}$. The particle is initially in the state

$$|\Psi\rangle = |2, 1, 0\rangle \ .$$

At time $t = 0$ a perturbation $\hat{P}(t)$, diagonal in the basis of the position eigenkets, is turned on:

$$\hat{P}(t)|\mathbf{r}\rangle = \lambda\frac{\delta(\phi-\omega t)}{\sin\theta\cos\theta}|\mathbf{r}\rangle$$

where θ and ϕ are the angles that determine $\mathbf{r}$ in polar coordinates and ω is a given frequency. The probability is asked for the lowest order in perturbation theory that at time $t < \frac{2\pi}{\omega}$ the particle can be found in the states $|n, 1, 1\rangle$.

Solution *To calculate the required probability we need to calculate the coefficient*

$$c_n(t) = -\frac{\mathrm{i}}{\hbar}\int_0^t dt'\langle n, 1, 1|\hat{P}(t)|2, 1, 0\rangle\ e^{\mathrm{i}(E_n-E_2)t'/\hbar}$$

$$= -\frac{\mathrm{i}}{\hbar}\int_0^t dt'\int_0^\infty dr\, r^2\int_0^\pi d\theta\sin\theta\int_0^{2\pi} d\phi\ R_{n,1}(r)Y^*_{1,1}(\theta,\phi)\frac{\delta(\phi-\omega t)}{\sin\theta\cos\theta}$$

$$\times\ R_{2,1}(r)Y_{1,0}(\theta,\phi)\ e^{\mathrm{i}(E_n-E_2)t'/\hbar}$$

The radial integral provides

$$\int_0^\infty dr\, r^2\ R_{n,1}(r)R_{2,1}(r) = \delta_{n,2}$$

as eigenfunctions corresponding to different eigenvalues are mutually orthogonal. Since $t < 2\pi/\omega$ *we have* $\omega t < 2\pi$ *and therefore* $\int_0^{2\pi} d\phi\ Y^*_{1,1}(\theta,\phi)\delta(\phi-\omega t)Y^*_{1,0}(\theta,\phi) = Y^*_{1,1}(\theta,\omega t)Y_{1,0}(\theta,\omega t)$. *Using the expressions given for spherical harmonics we arrive at the following result*

$$c_n(t) = -\delta_{n2}\frac{\mathrm{i}\lambda}{\hbar}\frac{3}{\sqrt{2}\,4\pi}\int_0^t dt' e^{-\mathrm{i}\omega t'}\int_0^\pi d\theta\sin\theta = -\delta_{n2}\frac{\mathrm{i}\lambda}{\hbar}\frac{6}{\sqrt{2}\,4\pi}e^{-\mathrm{i}\omega t/2}\frac{\sin\omega t/2}{\omega/2}$$

It follows that the required probability is

$$P_n(t) = |c_n(t)|^2 = \delta_{n2}\frac{36\lambda^2}{32\pi^2\hbar^2}\left(\frac{\sin\omega t/2}{\omega/2}\right)^2$$

13. A quantum system in one dimension is described by the Hamiltonian $\hat{H}_2 = \frac{1}{\hbar\omega}(\hat{H}_1 - \frac{5}{2}\hbar\omega)^2$, where $\hat{H}_1 = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$. Determine the correction to the energy of all levels of $\hat{H}$ to first order in perturbation theory due to the perturbing term $\lambda\hat{x}^2$.

Solution *Since $\hat{H}_2$ and $\hat{H}_1$ commute, the autokets $|n\rangle$ of $\hat{H}_1$ are also autokets of $\hat{H}_2$, with eigenvalues $E_n = \hbar\omega(n + \frac{1}{2} - \frac{5}{2})^2 = \hbar\omega(n-2)^2$.*

The ground state is non-degenerate and occurs for $n = 2$, and has energy $E_2 = 0$. The first and second excited states are obtained for $n = 1, 3$ (with $E_1 = E_3 = \hbar\omega$) and $n = 0, 4$ (with $E_0 = E_4 = 4\hbar\omega$) respectively, and they therefore have degeneracy two. Higher energy states have $n \geq 5$ and are not degenerate.

To see how these energy levels change due to the perturbation we must analyze the various cases.

- The ground state energy changes as

$$E_2 \to E_2 + \lambda\langle 2|\hat{x}^2|2\rangle = \frac{5}{2}\lambda x_0^2.$$

- To see how the first excited state is modified we need to diagonalize the 2 × 2 matrix

$$\mathbb{H} = \lambda\begin{pmatrix}\langle 1|\hat{x}^2|1\rangle & \langle 1|\hat{x}^2|3\rangle\\ \langle 3|\hat{x}^2|1\rangle & \langle 3|\hat{x}^2|3\rangle\end{pmatrix} = \lambda x_0^2\begin{pmatrix}3/2 & \sqrt{6}/2\\ \sqrt{6}/2 & 7/2\end{pmatrix}$$

whose eigenvalues are $\frac{\lambda x_0^2}{2}(5 \pm \sqrt{10})$. So the first excited state splits like

$$E_{1,3} \to \hbar\omega + \frac{\lambda x_0^2}{2}(5 \pm \sqrt{10})$$

- To see how the second excited state is modified we need to diagonalize the 2 × 2 matrix

$$\mathbb{H} = \lambda\begin{pmatrix}\langle 0|\hat{x}^2|0\rangle & \langle 0|\hat{x}^2|4\rangle\\ \langle 4|\hat{x}^2|0\rangle & \langle 4|\hat{x}^2|4\rangle\end{pmatrix} = \lambda x_0^2\begin{pmatrix}1/2 & 0\\ 0 & 9/2\end{pmatrix}$$

whose eigenvalues are $\frac{\lambda x_0}{2}$ and $\frac{9\lambda x_0}{2}$. So the second excited state splits like

$$E_{0,4} \to 4\hbar\omega + \left\{ \begin{array}{l} \frac{\lambda x_0}{2} \\ \frac{9\lambda x_0}{2} \end{array} \right.$$

- From the third excited state onwards, the energy of the levels change as

$$E_{n\geq 5} \to E_{n\geq 5} + \lambda\langle n|\hat{x}^2|n\rangle = \hbar\omega(n-2)^2 + \frac{2n+1}{2}\lambda x_0^2.$$

14. Consider a quantum harmonic oscillator in two dimensions described by the Hamiltonian

$$\hat{H} = \hat{H}_x + \hat{H}_y = \frac{\hat{p}_x^2}{2m} + \frac{m\omega^2\hat{x}^2}{2} + \frac{\hat{p}_y^2}{2m} + \frac{m\omega^2\hat{y}^2}{2}.$$

Calculate how the energies of the ground state and of the first two excited states change to first order in perturbation theory if it is turned on the perturbation $\hat{P} = \lambda\hat{x}^2\hat{y}^2$, where λ is a small parameter.

Solution *The Hamiltonian $\hat{H}$ is separable and therefore its eigenkets can be written as $|n_x, n_y\rangle = |n_x\rangle|n_y\rangle$, where $|n_x\rangle$ and $|n_y\rangle$ are the eigenkets of $\hat{H}_x$ and $\hat{H}_y$ respectively; the eigenvalues are instead $E_{n_x n_y} = \hbar\omega(n_x + n_y + 1)$ with n_x and n_y integers starting from zero. The first three levels are*

$$\begin{array}{ll} \hbar\omega = E_{0,0} & \text{degeneracy} = 1 \\ 2\hbar\omega = E_{1,0} = E_{0,1} & \text{degeneracy} = 2 \\ 3\hbar\omega = E_{2,0} = E_{1,1} = E_{0,2} & \text{degeneracy} = 3 \end{array}$$

Ground state correction: To correct the energy of the ground state which is non-degenerate we only need to calculate element

$$\langle 0, 0|\hat{P}|0.0\rangle = \lambda\langle 0_x|\hat{x}^2|0_x\rangle\langle 0_y|\hat{y}^2|0_y\rangle = \lambda\frac{x_0^4}{4}$$

where $x_0 = \sqrt{\frac{\hbar}{m\omega}}$. Therefore the ground state energy changes as

$$\hbar\omega \to \hbar\omega + \lambda\frac{x_0^4}{4}$$

First excited state correction: To correct the energy of the first excited state that is twice degenerate, we need to diagonalize the matrix

$$\begin{pmatrix} \langle 1.0|\hat{P}|1.0\rangle & \langle 1.0|\hat{P}|0.1\rangle \\ \langle 0, 1|\hat{P}|1.0\rangle & \langle 0.1|\hat{P}|0.1\rangle \end{pmatrix} = \lambda x_0^4 \begin{pmatrix} \frac{3}{4} & 0 \\ 0 & \frac{3}{4} \end{pmatrix}$$

Therefore the first excited state remains degenerate and its energy changes as

$$2\hbar\omega \to 2\hbar\omega + \frac{3}{4}\lambda x_0^4$$

Second excited state correction: To correct the energy of the second excited state that is three times degenerate, we need to diagonalize the matrix

$$\begin{pmatrix} \langle 2.0|\hat{P}|2.0\rangle & \langle 2.0|\hat{P}|1.1\rangle & \langle 2.0|\hat{P}|0.2\rangle \\ \langle 1,1|\hat{P}|2.0\rangle & \langle 1.1|\hat{P}|1,1\rangle & \langle 1,1|\hat{P}|0.2\rangle \\ \langle 0,2|\hat{P}|2.0\rangle & \langle 0.2|\hat{P}|1.1\rangle & \langle 0.2|\hat{P}|0.2\rangle \end{pmatrix} = \lambda x_0^4 \begin{pmatrix} \frac{5}{4} & 0 & \frac{1}{2} \\ 0 & \frac{9}{4} & 0 \\ \frac{1}{2} & 0 & \frac{5}{4} \end{pmatrix}$$

The above matrix is block diagonal and its eigenvalues are $\frac{3}{4}\lambda x_0^4$, $\frac{7}{4}\lambda x_0^4$ *and* $\frac{9}{4}\lambda x_0^4$. *Therefore the second excited level splits into three distinct levels*

$$3\hbar\omega \to \begin{cases} 3\hbar\omega + \frac{3}{4}\lambda x_0^4 \\ 3\hbar\omega + \frac{7}{4}\lambda x_0^4 \\ 3\hbar\omega + \frac{9}{4}\lambda x_0^4 \end{cases}$$

15. Consider a particle of mass m in one dimension in a potential well with infinitely high walls placed in $x = 0$ and $x = L$. The particle is in the ground state

$$\Psi_1(x) = \begin{cases} \sqrt{\frac{2}{L}}\sin(\frac{\pi x}{L}) & x \in (0, L) \\ 0 & \text{otherwise} \end{cases}$$

at time $t = 0$, when the perturbation

$$\hat{P}(t) = \lambda\delta(\hat{x} - \mathrm{v}t)$$

is turned on. Here $\mathrm{v} = \frac{3\pi\hbar}{2mL}$ is a constant with the physical dimension of a velocity. Calculate the probability of measuring energy $E_2 = \frac{\hbar^2}{2m}\frac{4\pi^2}{L^2}$ for a generic time $t > 0$ to lowest order in λ. Use the following notable results $\int dy\cos(y)\sin^3(y) = \frac{1}{4}\sin^4(y)$ and $\int dy\cos^2(y)\sin^2(y) = \frac{y}{8} - \frac{1}{32}\sin(4y)$.

Solution *To measure energy* E_2 *the particle must have non-zero probability to be in the first excited state*

$$\Psi_2(x) = \begin{cases} \sqrt{\frac{2}{L}}\sin(\frac{2\pi x}{L}) & x \in (0, L) \\ 0 & \text{otherwise} \end{cases}$$

This probability is given by the square modulus of the coefficient

$$c_2(t) = -\frac{\mathrm{i}\lambda}{\hbar}\int_0^t dt' \int_{-\infty}^{\infty} dx\ \Psi_2^*(x)\Psi_1(x)\delta(x-\mathrm{v}t)e^{\mathrm{i}\Omega_{21}t'}$$

with $\Omega_{21} = \frac{(E_2-E_1)}{\hbar} = \frac{3\pi^2\hbar}{2mL^2}$. *We therefore see that* $c_2(t) = 0$ for $t > L/\mathrm{v}$. *For* $t < L/\mathrm{v}$ *we have*

$$c_2(t) = -\frac{\mathrm{i}\lambda}{\hbar}\int_0^t dt'\Psi_2^*(\mathrm{v}t)\Psi_1(\mathrm{v}t)e^{\mathrm{i}\Omega_{21}t'} = -\frac{\mathrm{i}\lambda}{\hbar}\frac{2}{L}\int_0^t dt' \sin\left(\frac{2\pi\mathrm{v}t}{L}\right)\sin\left(\frac{\pi\mathrm{v}t}{L}\right)e^{\mathrm{i}\Omega_{21}t'}$$

We now observe that $\frac{\pi\mathrm{v}}{L} = \frac{3\pi^2\hbar}{2mL^2} = \Omega_{21}$. *Defining* $y = \Omega_{21}t'$ *we have*

$$\begin{aligned} c_2(t) &= -\frac{\mathrm{i}\lambda}{\hbar}\frac{2}{L\Omega_{21}}\int_0^{\Omega_{21}t} dy \sin(2y)\sin(y)\, e^{\mathrm{i}y} \\ &= -\frac{\mathrm{i}\lambda}{\hbar}\frac{4}{L\Omega_{21}}\int_0^{\Omega_{21}t} dy\cos(y)\sin^2(y)\left[\cos(y)+\mathrm{i}\sin(y)\right] \\ &= -\frac{\mathrm{i}\lambda}{\hbar}\frac{4}{L\Omega_{21}}\left[\frac{\Omega_{21}t}{8} - \frac{1}{32}\sin(4\Omega_{21}t) + \frac{\mathrm{i}}{4}\sin^4(\Omega_{21}t)\right] \end{aligned}$$

The asked probability is therefore

$$P(t) = |c_2(t)|^2 = \frac{\lambda^2}{\hbar^2L^2\Omega_{21}^2}\left[\left(\frac{\Omega_{21}t}{2} - \frac{1}{8}\sin(4\Omega_{21}t)\right)^2 + \frac{\sin^8(\Omega_{21}t)}{16}\right]$$

16. A particle of mass m in one dimension is described by the Hamiltonian $\hat{H} = \hat{H}_1 + \hat{H}_2$, where $\hat{H}_1$ is the Hamiltonian of a potential well with infinitely high walls

$$V(x) = \begin{cases} 0 & \text{per} \quad -L/2 < x < L/2 \\ \infty & \text{otherwise} \end{cases}$$

which has eigenkets $|\phi_n\rangle$, while $\hat{H}_2 = 3\epsilon_0(|\phi_1\rangle\langle\phi_3| + |\phi_3\rangle\langle\phi_1|)$, with $\epsilon_0 = \frac{\hbar^2}{2mL^2}$. The system is initially in the ground state of $\hat{H}$, and at time $t = 0$ the perturbation is turned on $\hat{P}(t) = \lambda\hat{x}^2\cos\omega t$, with $\omega > 0$.

Determine to the lowest order in λ the lowest energy excited state of $\hat{H}$ towards which the system can transit and the corresponding probability per unit time for $t \to \infty$.

Solution *We define* $|\psi_m\rangle$ *and* E_m *eigenkets and eigenvalues of* $\hat{H}$. *Since* $\hat{H}_2$ *involves only states with* $n = 1$ *ed* $n = 3$, *the kets* $|\phi_m\rangle = |\psi_m\rangle$ *with* $m \neq 1, 3$ *are also eigenkets of* $\hat{H}$ *with eigenvalues* $E_m = \epsilon_m = \epsilon_0 m^2$. *To determine how*

$|\phi_1\rangle$ and $|\phi_3\rangle$ mix to obtain eigenkets of $\hat{H}$, one must diagonalize the 2×2 matrix

$$h = \begin{pmatrix} \langle\phi_1|\hat{H}|\phi_1\rangle & \langle\phi_1|\hat{H}|\phi_3\rangle \\ \langle\phi_3|\hat{H}|\phi_1\rangle & \langle\phi_3|\hat{H}|\phi_3\rangle \end{pmatrix} = \epsilon_0 \begin{pmatrix} 1 & 3 \\ 3 & 9 \end{pmatrix}. \tag{6.75}$$

From the eigenvectors of h we find that the 2 missing eigenkets of $\hat{H}$ are $|\psi_1\rangle = \frac{1}{\sqrt{10}}(3|\phi_1\rangle - |\phi_3\rangle)$ and $|\psi_3\rangle = \frac{1}{\sqrt{10}}(|\phi_1\rangle + 3|\phi_3\rangle)$, with energies $E_1 = 0$ and $E_3 = 10\epsilon_0$ respectively. Therefore the ground state of $\hat{H}$ is $|\psi_1\rangle$ and has energy E_1.

The perturbation $\hat{P}(t)$ can be rewritten as $\hat{P}(t) = \lambda(\frac{\hat{x}^2}{2}e^{\mathrm{i}\omega t} + \frac{\hat{x}^2}{2}e^{-\mathrm{i}\omega t})$, and therefore we can use Fermi's golden rule. The transition rate towards a generic excited state $|\psi_m\rangle$ of $\hat{H}$ is

$$\lim_{t\to\infty} \frac{|c_m|^2}{t} = \lambda^2 \frac{2\pi}{\hbar}|A_{m1}|^2 \delta(E_m - E_1 - \hbar\omega) \tag{6.76}$$

where

$$A_{m1} = \langle\psi_m|\frac{\hat{x}^2}{2}|\psi_1\rangle = \int_{-L/2}^{L/2} dx\, \psi_m^*(x) \left(\frac{x^2}{2}\right) \psi_1(x). \tag{6.77}$$

Since $\psi_1(x)$ is an even function and the other eigenfunctions $\psi_m(x)$ have definite parity, the integral is non-zero only if $\psi_m(x)$ is also an even function. The lowest energy even excited state is $|\psi_3\rangle$, and therefore the integral to be calculated is

$$\begin{aligned} A_{31} &= \int_{-L/2}^{L/2} dx\, \psi_3^*(x) \left(\frac{x^2}{2}\right) \psi_1(x) \\ &= \frac{3}{20}\int_{-L/2}^{L/2} dx\, \phi_1^2(x)x^2 - \frac{3}{20}\int_{-L/2}^{L/2} dx\, \phi_3^2(x)x^2 + \frac{8}{20}\int_{-L/2}^{L/2} dx\, \phi_1(x)\phi_3(x)x^2 \\ &= \frac{2L^2}{\pi^3}(\frac{3}{20}I_1 - \frac{3}{20}I_2 + \frac{8}{20}I_3) = -\frac{13}{120}\frac{L^2}{\pi^2}. \end{aligned} \tag{6.78}$$

Therefore the rate of the transition towards the state $|\psi_3\rangle$ is

$$\lim_{t\to\infty} \frac{|c_3|^2}{t} = \lambda^2 \frac{2\pi}{\hbar}\frac{L^4}{\pi^4}\left(\frac{13}{120}\right)^2 \delta(10\epsilon_0 - \omega) \tag{6.79}$$

17. Consider a one-dimensional quantum harmonic oscillator of frequency ω and mass m. So the particle is described by the Hamiltonian $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 = \hbar\omega(\hat{a}^\dagger\hat{a} + \frac{1}{2})$. At time $t = 0$ the system is prepared in the state

$$|\Psi\rangle = C\left(e^{-\frac{\gamma^2}{2}}|0\rangle - \sum_{n=0}^{\infty} e^{-\frac{\gamma^2}{2}}\frac{\gamma^n}{\sqrt{n!}}|n\rangle\right), \tag{6.80}$$

with γ a real constant. The kets $|n\rangle$, $n \geq 0$, are the eigenkets of $\hat{H}$ with eigenvalue $\hbar\omega(n+\frac{1}{2})$.
i. Find the constant C so that the state $|\Psi\rangle$ is normalized to one.
ii. If at time $t = 0$ the weak perturbation $\lambda\hat{P}(t)$ is turned on with $\lambda \ll 1$ and $\hat{P}(t) = \hat{x}\sin(\omega t)$, what is the probability that at time $t = \pi/\omega$ a measure of energy provides the value $\hbar\omega/2$? Determine the result to lowest order in λ.

Solution *i. The state* $|\Psi\rangle = e^{-\frac{\gamma^2}{2}}|0\rangle - |\Phi_\gamma\rangle$ *with* $|\Phi_\gamma\rangle$ *the coherent state normalized to unity. Taking into account that* γ *is real we have* $\langle\Psi|\Psi\rangle = e^{-\gamma^2} + 1 - 2e^{-\gamma^2} = 1 - e^{-\gamma^2}$.
ii. It is necessary to calculate the probability that at a generic time $t > 0$ *the system is in the ground state of the harmonic oscillator. From the theory of time-dependent perturbations, such probability is obtained by calculating the square modulus of the coefficient*

$$c_0(t) = c_0(0) - \frac{\mathrm{i}\lambda}{\hbar}\sum_{n=0}^{\infty}\int_0^t dt'\langle 0|\hat{x}\sin(\omega t')|n\rangle e^{\mathrm{i}\frac{E_0-E_n}{\hbar}t'}c_n(0),$$

where $c_0(0) = 0$, $c_n(0) = -\frac{e^{-\frac{\gamma^2}{2}}}{\sqrt{1-e^{-\gamma^2}}}\frac{\gamma^n}{\sqrt{n!}}$ *for* $n > 0$ *and* $E_n = \hbar\omega(n + 1/2)$. *Remembering that* $\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a} + \hat{a}^\dagger)$ *you see immediately that only the term with to* $n = 1$ *survives in the sum. Therefore*

$$\begin{aligned} c_0(t) &= \frac{\mathrm{i}\lambda}{\hbar}\sqrt{\frac{\hbar}{2m\omega}}\frac{e^{-\frac{\gamma^2}{2}}}{\sqrt{1-e^{-\gamma^2}}}\gamma\int_0^t dt'\sin(\omega t')e^{-\mathrm{i}\omega t'} \\ &= \frac{e^{-\frac{\gamma^2}{2}}}{\sqrt{1-e^{-\gamma^2}}}\frac{\mathrm{i}\lambda\gamma}{\sqrt{2m\hbar\omega}}\frac{1-e^{-2\mathrm{i}\omega t}-2\mathrm{i}\omega t}{4\omega}. \end{aligned}$$

The required probability is then given by

$$P = |c_0(\pi/\omega)|^2 = \frac{e^{-\gamma^2}}{1-e^{-\gamma^2}}\frac{\lambda^2\pi^2\gamma^2}{8m\hbar\omega^3}$$

18. Consider a quantum harmonic oscillator in one dimension described by the Hamiltonian $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2\hat{x}^2}{2}$. At time $t = 0$ the system is in the first excited state of $\hat{H}$, and is subjected to the perturbation $\hat{P}(t) = \lambda\hat{x}^3e^{-\eta t}$, where λ is a small parameter and η is a positive constant.

Calculate to the lowest order in λ the probability that at time t the system decays into ground state of $\hat{H}$.

Solution *The probability is* $P(t) = |c_0(t)|^2$, *where the coefficient* $c_0(t)$ *is obtained from time-dependent perturbation theory as*

$$c_0(t) = -\frac{\mathrm{i}\lambda}{\hbar}\int_0^t dt' P_{01}(t') e^{\mathrm{i}\frac{E_0-E_1}{\hbar}t'},$$

with $E_0 = \frac{\hbar\omega}{2}$, $E_1 = \frac{3\hbar\omega}{2}$ *and* $P_{01}(t) = \langle 0|\hat{x}^3|1\rangle e^{-\eta t}$. *First we need to calculate* $\langle 0|\hat{x}^3|1\rangle$, *where we recall that* $\hat{x} = \frac{x_0}{\sqrt{2}}(\hat{a} + \hat{a}^\dagger)$, *with* $x_0 = \sqrt{\frac{\hbar}{m\omega}}$. *Using the properties of the operators* $\hat{a}$ *and* $\hat{a}^\dagger$ *the only terms that survive for the calculation of the matrix element are*

$$\langle 0|\hat{x}^3|1\rangle = \frac{x_0^3}{2^{3/2}}\langle 0|(\hat{a}^2\hat{a}^\dagger + \hat{a}\hat{a}^\dagger\hat{a})|1\rangle = \frac{x_0^3}{2^{3/2}}(2+1) = \frac{3x_0^3}{2^{3/2}}.$$

Therefore the coefficient $c_0(t)$ *reads*

$$c_0(t) = -\frac{3\mathrm{i}\lambda x_0^3}{2^{3/2}\hbar}\int_0^t dt' e^{-\eta t'} e^{-\mathrm{i}\omega t'} = -\frac{3\mathrm{i}\lambda x_0^3}{2^{3/2}\hbar}\frac{1 - e^{-t(\eta + \mathrm{i}\omega)}}{\eta + \mathrm{i}\omega},$$

which yields the probability

$$P(t) = \frac{9\lambda^2 x_0^6}{8\hbar^2}\frac{1 + e^{-2\eta t} - 2e^{-\eta t}\cos\omega t}{\omega^2 + \eta^2}$$

19. A quantum system in two dimensions is subject to the potential

$$\hat{V}(x_1, x_2) = \begin{cases} 0 & \text{per} \quad 0 < x_1 < L \quad \text{e} \quad 0 < x_2 < \sqrt{\frac{3}{8}}L \\ \infty & \text{otherwise} \end{cases}$$

i. Determine the energies of the first 3 levels of the system.
ii. Determine how these energies are corrected in first order perturbation theory due to the disturbing potential $\hat{P} = \lambda\ (\hat{x}_2 - \sqrt{\frac{3}{32}}L)\ \delta(\hat{x}_1 - \frac{L}{2})$.

Solution *i. The Hamiltonian of the system is separable into a part* $\hat{H}_1$ *which depends only on* x_1 *(an infinite potential well of width* $L_1 = L$*) and a part* $\hat{H}_2$ *which depends only on* x_2 *(an infinite potential well of width* $L_2 = \sqrt{\frac{3}{8}}L$*). The eigenvalues and eigenfunctions of* $\hat{H}_i$ *are therefore* $\epsilon_n^{(i)} = \frac{\pi^2\hbar^2}{2m}\frac{n^2}{L_i^2}$ *and*

$\psi_n^{(i)}(x_i) = \sqrt{\frac{2}{L_i}} \sin\left(\frac{n\pi x_i}{L_i}\right)$, *with* $i = 1, 2$. *The first three levels of the system and their respective eigenfunctions are:*

$$\begin{aligned}
E_1 &\equiv \epsilon_1^{(1)} + \epsilon_1^{(2)} = \frac{\pi^2\hbar^2}{2m}\frac{1}{L^2}\left(1 + \frac{8}{3}\right) = \frac{\pi^2\hbar^2}{2m}\frac{11}{3L^2} \quad , \quad \Psi_1(x_1, x_2) = \psi_1^{(1)}(x_1)\psi_1^{(2)}(x_2) \\
E_2 &\equiv \epsilon_2^{(1)} + \epsilon_1^{(2)} = \frac{\pi^2\hbar^2}{2m}\frac{1}{L^2}\left(4 + \frac{8}{3}\right) = \frac{\pi^2\hbar^2}{2m}\frac{20}{3L^2} \quad , \quad \Psi_2(x_1, x_2) = \psi_2^{(1)}(x_1)\psi_1^{(2)}(x_2) \\
E_3 &\equiv \epsilon_3^{(1)} + \epsilon_1^{(2)} = \frac{\pi^2\hbar^2}{2m}\frac{1}{L^2}\left(9 + \frac{8}{3}\right) = \frac{\pi^2\hbar^2}{2m}\frac{35}{3L^2} \quad , \quad \Psi_{3a}(x_1, x_2) = \psi_3^{(1)}(x_1)\psi_1^{(2)}(x_2) \\
&\equiv \epsilon_1^{(1)} + \epsilon_2^{(2)} = \frac{\pi^2\hbar^2}{2m}\frac{1}{L^2}\left(1 + \frac{4 \cdot 8}{3}\right) = \frac{\pi^2\hbar^2}{2m}\frac{35}{3L^2} \quad , \quad \Psi_{3b}(x_1, x_2) = \psi_1^{(1)}(x_1)\psi_2^{(2)}(x_2)
\end{aligned}$$

Therefore the level E_3 *is twice degenerate, while* E_1 *and* E_2 *are not degenerate.*

ii. Let's calculate the correction to E_1:

$$\begin{aligned}
\Delta E_1 &= \lambda \int dxdy\, |\Psi_1(x, y)|^2 \delta(x - \frac{L}{2}) \times (y - \sqrt{\frac{3}{32}}L) \\
&= \lambda \int_0^L dx\, |\psi_1^{(1)}(x)|^2 \delta(x - \frac{L}{2}) \int_0^{\sqrt{\frac{3}{8}}L} dy\, |\psi_1^{(2)}(y)|^2 (y - \sqrt{\frac{3}{32}}L) = 0
\end{aligned}$$

In fact, the integral in the variable y *vanishes due to parity since* $|\psi_1(y)|^2$ *is even with respect to the point* $\sqrt{\frac{3}{32}}L$, *while the function* $(y - \sqrt{\frac{3}{32}}L)$ *is odd with respect to same point. With similar reeasonings one can show that also* $\Delta E_2 = 0$.

To calculate the correction to E_3 *we need to use first order perturbation theory in the degenerate case. In particular, we have to diagonalize the matrix* P *of elements*

$$P_{ij} = \lambda \int dxdy\, \Psi_{3i}(x, y)^* \left[\delta(x - \frac{L}{2}) \times (y - \sqrt{\frac{3}{32}}L)\right] \Psi_{3j}(x, y) \quad \text{con} \quad i, j = a, b$$

For the symmetry reason mentioned before we have $P_{11} = P_{22} = 0$. *Calculating* $P_{12} = P_{21}$ *provides instead*

$$\begin{aligned}
P_{12} &= \lambda \int_0^L right\, \psi_1^{(1)}(x)\psi_3^{(1)}(x)\delta(x - \frac{L}{2}) \int_0^{\sqrt{\frac{3}{8}}L} dy\, \psi_1^{(2)}(y)\psi_2^{(2)}(y)(y - \sqrt{\frac{3}{32}}L) \\
&= \frac{4\lambda}{3\pi^2 L^2}\left(\frac{8}{3}\right)^{\frac{1}{2}}
\end{aligned}$$

The eigenvalues of the matrix P are simply $\pm P_{12}$, and therefore the perturbation removes the degeneracy so that $E_3 \to E_3 \pm \frac{4\lambda}{3\pi^2 L^2}\left(\frac{8}{3}\right)^{\frac{1}{2}}$.

20. A particle of mass m in one dimension is described by Hamiltonian

$$\hat{H} = -\epsilon_1 |\varphi_1\rangle\langle\varphi_1| + \sum_{n=1}^{\infty} \epsilon_n |\varphi_n\rangle\langle\varphi_n|$$

where $\epsilon_n = n^2 \frac{\pi^2\hbar^2}{2mL^2}$ and $|\varphi_n\rangle$, $n = 1, 2, 3, \ldots$ are the eigenvalues and eigenkets of another Hamiltonian corresponding to an infinite-walled potential well located between 0 and L. Consider the small perturbation $\lambda\hat{P} = \lambda\delta(\hat{x} - L/2)$. Calculate

i. The unperturbed eigenkets and eigenvalues of $\hat{H}$

ii. The eigenfunctions $\langle x|\varphi_n\rangle$

ii. The first order correction in λ of all eigenvalues of $\hat{H}$

iii. The second order correction in λ of the lowest eigenvalue of $\hat{H}$. To this end, use the notable result $\sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} = \frac{\pi^2}{8}$.

Solution *i. The eigenkets of $\hat{H}$ are the $|\varphi_n\rangle$. We denote by E_n the corresponding eigenvalues. We have $E_1 = 0$ and $E_n = \epsilon_n = n^2\epsilon_1$ for all $n \geq 2$*
ii. From perturbation theory the first order correction of the level E_n is given by

$$E_n^{(1)} = \lambda\langle\varphi_n|\delta(\hat{x} - L/2)|\varphi_n\rangle = \lambda\frac{2}{L}\int_0^L dx \sin^2\left(\frac{n\pi x}{L}\right)\delta(x - L/2) = \lambda\frac{2}{L}\sin^2\left(\frac{n\pi}{2}\right)$$

$$= \begin{cases} \lambda\frac{2}{L} & n \text{ odd} \\ 0 & n \text{ even} \end{cases}$$

iii. From perturbation theory the second order correction of the level E_1 is given by

$$E_1^{(2)} = \lambda^2 \sum_{m=2}^{\infty} \frac{|\langle\varphi_1|\delta(\hat{x} - L/2)|\varphi_m\rangle|^2}{E_1 - E_m}$$

$$= -\lambda^2\left(\frac{2}{L}\right)^2 \frac{1}{\epsilon_1}\sum_{m=2}^{\infty}\frac{\sin^2(\frac{m\pi}{2})}{m^2} = -\frac{\lambda^2 8m}{\pi^2\hbar^2}\left(\frac{1}{3^2} + \frac{1}{5^2} + \frac{1}{7^2} + \ldots\right) = -\frac{\lambda^2 m}{\pi^2\hbar^2}(\pi^2 - 8)$$

21. Consider a particle in the ground state of the Hamiltonian of the harmonic oscillator $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$. At time $t = 0$ the particle is subject to one of the following perturbations

$$\hat{P}_1 = \lambda\hat{x}^2\hat{p}^2\hat{x}^2, \quad \hat{P}_2 = \lambda\hat{x}^2\hat{p}\,\hat{x}^2\hat{p}. \quad \hat{P}_3 = \lambda\,\hat{p}^2\hat{x}^4, \quad \hat{P}_4 = \lambda\,\hat{p}\,\hat{x}^4\hat{p}, \quad \hat{P}_5 = \lambda\,\hat{p}\,\hat{x}^2\hat{p}\,\hat{x}\,\hat{p}\,\hat{x},$$

i. Determine which of these perturbations is a Hermitian operator
ii. For Hermitian perturbations only calculate to lowest order in perturbation theory the probability that at time $t = \pi/(6\hbar\omega)$ the particle is in the sixth excited state of $\hat{H}$. The calculation must be done for one perturbation at a time.

Solution *i. The only Hermitian perturbations are* $\hat{P}_1$ *e* $\hat{P}_4$.
ii. In terms of the raising and lowering operators they can be written as

$$\hat{P}_1 = -\frac{\lambda}{2^3}\frac{\hbar^3}{m\omega}(\hat{a}+\hat{a}^\dagger)^2(\hat{a}-\hat{a}^\dagger)^2(\hat{a}+\hat{a}^\dagger)^2 \quad , \quad \hat{P}_4 = -\frac{\lambda}{2^3}\frac{\hbar^3}{m\omega}(\hat{a}-\hat{a}^\dagger)(\hat{a}+\hat{a}^\dagger)^4(\hat{a}-\hat{a}^\dagger)$$

To first order in perturbation theory the probability amplitude of transitioning to the sixth excited state is

$$c_6(t) = -\frac{\mathrm{i}}{\hbar}\int_0^t dt'\langle 6|\hat{P}|0\rangle e^{\mathrm{i}6\hbar\omega t'}$$

where the calculation must be performed both with $\hat{P} = \hat{P}_1$ *and with* $\hat{P} = \hat{P}_4$. *In both cases the only non-zero terms are those proportional to* $(\hat{a}^\dagger)^6$. *Remembering that* $(\hat{a}^\dagger)^6|0\rangle = \sqrt{6!}|6\rangle$ *we have that for both the perturbations*

$$c_6(t) = \frac{\mathrm{i}}{\hbar}\frac{\lambda}{2^3}\frac{\hbar^3}{m\omega}\sqrt{6!}\int_0^t dt' e^{\mathrm{i}6\hbar\omega t'} = \frac{\mathrm{i}}{\hbar}\frac{\lambda}{2^3}\frac{\hbar^3}{m\omega}\sqrt{6!}\,\frac{e^{\mathrm{i}6\hbar\omega t}-1}{\mathrm{i}6\hbar\omega}.$$

The probability at the required time is therefore $P = |c_6(\frac{\pi}{6\hbar\omega})|^2 = (\lambda\frac{\hbar}{m\omega^2}\frac{\sqrt{5!}}{4})^2$.

22. A particle of spin 1/2, mass m and charge e is described by the Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} - \frac{e^2}{\hat{r}} + \frac{\hat{L}^2}{2I}$$

where $I = \frac{72}{5}\frac{\hbar^4}{me^4}$.
i. Determine the first 3 levels of $\hat{H}$ and their degeneracy.
ii. Determine how the degeneracy of the first 3 levels is lifted by the perturbation $\hat{P} = \alpha\hat{L}_z$.
iii. Determine how the degeneracy of the first 3 levels is lifted by the perturbation $\hat{P} = \beta\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}$

Solution *i.The Hamiltonian of the hydrogen atom* $\frac{\hat{p}^2}{2m} - \frac{e^2}{\hat{r}}$ *and of the isotropic quantum rotator* $\frac{\hat{L}^2}{2I}$ *commute, and we can consider them both diagonal on the basis* $|n, l, m; \frac{1}{2}m_s\rangle$. *Therefore the eigenvalues of* $\hat{H}$ *are* $E_{nl} = -\frac{me^4}{2\hbar^2 n^2} + \frac{\hbar^2 l(l+1)}{2I}$ *with* $l = 1, 2 \ldots n-1$. *The first three levels are*

$$
\begin{aligned}
E_{10} &= -\frac{me^4}{2\hbar^2} \equiv E_1 \quad \text{degeneracy} \;\; 2 \\
E_{20} &= -\frac{me^4}{8\hbar^2} \equiv E_2 \quad \text{degeneracy} \;\; 2 \\
E_{21} = E_{30} &= -\frac{me^4}{18\hbar^2} \equiv E_3 \quad \text{degeneracy} \;\; 8
\end{aligned}
$$

ii. The perturbation $\alpha\hat{L}_z$ is diagonal on the eigenstates of $\hat{H}$. It is immediate to verify that this perturbation does not lift the twofold degeneracy of E_1 and E_2, while it lifts the degenracy of the second excited state E_3. In particular we have

$$
\begin{aligned}
&E_3 \to E_3 - \alpha\hbar \quad \text{per} \quad |2,1,-1;\frac{1}{2} \pm \frac{1}{2}\rangle \quad \text{degeneracy} \;\; 2 \\
&E_3 \to E_3 \quad \text{per} \quad |2,1,0;\frac{1}{2} \pm \frac{1}{2}\rangle \quad \text{e} \quad |3,0,0;\frac{1}{2} \pm \frac{1}{2}\rangle \quad \text{degeneracy} \;\; 4 \\
&E_3 \to E_3 + \alpha\hbar \quad \text{per} \quad |2,1,1;\frac{1}{2} \pm \frac{1}{2}\rangle \quad \text{degeneracy} \;\; 2
\end{aligned}
$$

iii. The perturbation $\beta\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ does not lift the twofold degeneracy of E_1 and E_2 since their respective states have $l = 0$. As regards the E_3 level, however, it is split into three sublevels. In particular the 2 states $|3,0,0;\frac{1}{2} \pm \frac{1}{2}\rangle$ of the octet are not affected by the perturbation since they also have $l = 0$. The perturbation is not diagonal on the remaining 6 states with $l = 1$ $|2,1,m;\frac{1}{2} \pm \frac{1}{2}\rangle$ (where $m = -1,0,1$). To diagonalize it, it is conveninet to work in the basis of the eigenstates of total angular momentum, $|2,\frac{1}{2},m_j\rangle_{1\frac{1}{2}}$ ($m_j = \pm 1/2$) and $|2,\frac{3}{2},m_j\rangle_{1\frac{1}{2}}$ ($m_j = -3/2,-1/2,1/2,3/2$). Therefore

$$
\begin{aligned}
&E_3 \to E_3 \quad \text{per} \quad |3,0,0;\frac{1}{2} \pm \frac{1}{2}\rangle \quad \text{degeneracy} \;\; 2 \\
&E_3 \to E_3 - \beta\hbar^2 \quad \text{per} \quad |2,\frac{1}{2},\pm\frac{1}{2}\rangle_{1\frac{1}{2}} \quad \text{degeneracy} \;\; 2 \\
&E_3 \to E_3 + \frac{\beta\hbar^2}{2} \quad \text{per} \quad |2,\frac{3}{2},m_j\rangle_{1\frac{1}{2}} \quad \text{con} \quad m_j = -3/2,-1/2,1/2,3/2 \quad \text{degenerazione} \;\; 4
\end{aligned}
$$

23. Consider a one-dimensional quantum harmonic oscillator of frequency ω and let $|n\rangle$, with $n = 0,1,2,\ldots$, be the eigenstates of energy $E_n = \hbar\omega(n + 1/2)$. The Hamiltonian can therefore be written as $\hat{H} = \sum_{n\geq 0} E_n |n\rangle\langle n|$. Let the small perturbation be given

$$
\hat{P} = \lambda\hbar\omega \sum_{n>0} \sqrt{\frac{v^n}{(n-1)!}} \big(|n\rangle\langle 0| + |0\rangle\langle n|\big)
$$

with $\lambda \ll 1$ and v a numerical constant greater than zero. Determine the ground state energy correction to the first and second order in λ. Determine for which values of v the corrected eigenvalue is zero.

Solution *To first order we have* $E_0^{(1)} = \langle 0|\hat{P}|0\rangle = 0$. *To second order we have* $E_0^{(2)} = -\sum_{n>0} |\langle 0|\hat{P}|n\rangle|^2/(n\hbar\omega)$. *Since* $\langle 0|\hat{P}|n\rangle = \lambda\hbar\omega\sqrt{\frac{v^n}{(n-1)!}}$ *we have*

$$E_0^{(2)} = -\sum_{n>0} \frac{(\lambda\hbar\omega)^2 v^n}{\hbar\omega n!} = -\lambda^2\hbar\omega(e^v - 1)$$

The corrected eigenvalue is therefore $E = \hbar\omega\Big(\frac{1}{2} - \lambda^2(e^v - 1)\Big)$, *which vanishes for* $v = \ln\big(1 + \frac{1}{2\lambda^2}\big)$.

More Exercises

24. The Hamiltonian of the harmonic oscillator $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$ is subject to the perturbation $\hat{P} = \lambda(b\hat{x} + c)$ where b and c are real constants.
i. Calculate the exact eigenvalues of $\hat{H} + \hat{P}$
ii. Treating $\hat{P}$ as a perturbation compute the correction up to the second order in λ of the unperturbed energies of $\hat{H}$.
iii. Are the exact eigenvalues the same as the perturbed ones? If so, why?
25. A particle of mass m in two dimensions is described by the Hamiltonian

$$\hat{H} = \frac{\hat{p}_x^2 + \hat{p}_y^2}{2m} + \frac{1}{2}m(\omega_x^2\hat{x}^2 + \omega_y^2\hat{y}^2) + V(e^{\lambda\hat{\rho}} - 1)$$

where $\hat{\rho} = \hat{a}_x\hat{a}_y + \hat{a}_x^\dagger\hat{a}_y^\dagger$ is expressed in terms of the raising and lowering operators along the x and y directions (e.g., $\hat{a}_x = \sqrt{\frac{m\omega_x}{2\hbar}}\hat{x} + \mathrm{i}\frac{\hat{p}_x}{\sqrt{2m\hbar\omega_x}}$).
i. Calculate the correction to the ground state energy up to second order in λ.
ii. Determine the value of V such that the correction calculated in the previous point is zero.
26. A particle of mass m is confined in one dimension between 0 and L by an infinite-walled potential well. The following perturbation is then added to the potential well: $V(x) = \lambda\cos(\frac{\pi x}{L})\theta(x)\theta(\frac{L}{2} - x)$. Calculate the correction to the energy of the ground state and the first excited state to first order in λ.
27. Let a quantum system be described by the Hamiltonian $\hat{H}$ with eigenkets $|n\rangle$ with $n = 0, 1, 2, \ldots$. The corresponding eigenvalues E_n are given by

$$E_n = \begin{cases} 0 & n = 0 \\ Qn! & n > 0 \end{cases}$$

with $Q > 0$.

i. Calculate the first- and second-order corrections in $\lambda > 0$ to the ground state energy due to the perturbation

$$\hat{P} = \lambda \sum_{m=0}^{\infty} \alpha^{m/2} (|m\rangle\langle 0| + |0\rangle\langle m|)$$

ii. For which values of α does the sum of the correction of the first e second order cancel?

28. The electron of a Hydrogen atom is in the ground state and is therefore described by the wavefunction $\Psi(\mathbf{r}) = \frac{2}{\sqrt{4\pi}} \left(\frac{1}{a_{\mathrm{B}}}\right)^{\frac{3}{2}} e^{-r/a_{\mathrm{B}}}$ with a_{B} the Bohr radius. Calculate to first order in perturbation theory the correction to the energy of the ground state due to the presence of the small perturbation $\hat{P} = \lambda e^{2\hat{r}/a_{\mathrm{B}} - (\hat{r}/a_{\mathrm{B}})^2}$.
29. A system described by the Hamiltonian of the harmonic oscillator $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2$ is found in the ground state $|0\rangle$. The oscillator is exposed to the perturbation $\hat{P}(t) = QE(t)\hat{x}$ where Q is the charge of the particle and $E(t) = E_0(e^{\mathrm{i}\omega t} + e^{-\mathrm{i}\omega t})$ is the electric field. Calculate to first order in E_0 the probability of measuring energy $3\hbar\omega/2$ at time t.

Appendix A
Dirac Delta: Definition and Properties

The Dirac delta function $\delta(x)$ is a function (or more precisely, a limit function) such that

$$\int dx' f(x')\delta(x-x') = f(x) \tag{A.1}$$

for any function f. Let us divide the real axis into intervals of length Δ and define the points $x_n = n\Delta$. As Δ decreases, the points x_n become increasingly close to each other, and in the limit $\Delta \to 0$, we obtain all points on the real axis. We use the definition of the integral to rewrite Eq. (A.1) as:

$$\int dx' f(x')\delta(x_n - x') = \lim_{\Delta\to 0}\sum_{n'} \Delta f(x_{n'})\delta(x_n - x_{n'}) = f(x_n). \tag{A.2}$$

From the last identity, we see that the Dirac delta can then be written as

$$\delta(x_n - x_{n'}) = \lim_{\Delta\to 0}\frac{\delta_{n,n'}}{\Delta}. \tag{A.3}$$

We can use this result to obtain an important representation of the Dirac delta.

Consider the sum

$$\sum_{k=0}^{N-1} z^k = \frac{1-z^N}{1-z} \tag{A.4}$$

where z can be any complex number. We choose $z = e^{\frac{2\pi i}{N}j}$ with j being an integer. If j is a multiple of N, then $z = 1$, and the sum yields N. If, on the other hand, j is not a multiple of N, then, since $z^N = e^{2\pi i j} = 1$, the sum is zero. Therefore, we can write:

$$\sum_{k=0}^{N-1} e^{\frac{2\pi \mathrm{i}}{N}jk} = N(\ldots\delta_{j,-N} + \delta_{j,0} + \delta_{j,N} + \delta_{j,2N} + \cdots) \tag{A.5}$$

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Multiplying this equation by $e^{-\frac{2\pi \mathrm{i}}{N} j \frac{N}{2}} = e^{-\pi \mathrm{i} j}$ we find

$$\begin{aligned}\sum_{k=0}^{N-1} e^{\frac{2\pi \mathrm{i}}{N} j (k-\frac{N}{2})} &= N e^{-\pi \mathrm{i} j} (\ldots \delta_{j,-N} + \delta_{j,0} + \delta_{j,N} + \delta_{j,2N} + \cdots) \\ &= N(\ldots e^{\pi \mathrm{i} N} \delta_{j,-N} + \delta_{j,0} + e^{-\pi \mathrm{i} N} \delta_{j,N} + e^{-2\pi \mathrm{i} N} \delta_{j,2N} + \cdots) \end{aligned} \tag{A.6}$$

If we choose N to be an even number, then all the exponentials multiplying the Kronecker deltas are equal to 1. By changing the index of the sum to $k' = k - N/2$ and renaming k' as k, we can rewrite the equation above as

$$\sum_{k=-N/2}^{N/2-1} e^{\frac{2\pi \mathrm{i}}{N} jk} = N(\ldots \delta_{j,-N} + \delta_{j,0} + \delta_{j,N} + \delta_{j,2N} + \cdots). \tag{A.7}$$

We divide this equation by N and define $\Delta = 1/N$:

$$\Delta \sum_{k=-N/2}^{N/2-1} e^{\frac{2\pi \mathrm{i}}{N} jk} = \ldots \delta_{j,-N} + \delta_{j,0} + \delta_{j,N} + \delta_{j,2N} + \cdots \tag{A.8}$$

Now, let us consider the points on the real axis, $q_k = k\Delta = k/N$. In the limit $N \to \infty$, and thus $\Delta \to 0$, the sum becomes an integral over the continuous variable q. Since the minimum value of q_k is $-1/2$ and the maximum value is $1/2$, the integration limits are $-1/2$ and $1/2$. Considering that in the limit $N \to \infty$, the only Kronecker delta that can be nonzero is $\delta_{j,0}$, we find

$$\int_{-1/2}^{1/2} dq\, e^{2\pi \mathrm{i} jq} = \delta_{j,0}. \tag{A.9}$$

Now we divide this equation by Δ and define the points on the real axis as $x_j = j\Delta$:

$$\frac{1}{\Delta} \int_{-1/2}^{1/2} dq\, e^{2\pi \mathrm{i} \frac{q}{\Delta} x_j} = \frac{\delta_{j,0}}{\Delta}. \tag{A.10}$$

Making the variable change $p = 2\pi q/\Delta$ and thus $dp = 2\pi dq/\Delta$, we can rewrite this equation as:

$$\int_{-\pi/\Delta}^{\pi/\Delta} \frac{dp}{2\pi}\, e^{\mathrm{i} p x_j} = \frac{\delta_{j,0}}{\Delta}. \tag{A.11}$$

Now, taking the limit $\Delta \to 0$ and considering Eq. (A.3), we obtain the following representation of the Dirac delta:

$$\int_{-\infty}^{\infty} \frac{dp}{2\pi}\, e^{\mathrm{i}px_j} = \delta(x_j). \tag{A.12}$$

Since this identity must hold for every x_j, we can set $x_j = (x - x')$ and rewrite the above result in a more familiar form

$$\int_{-\infty}^{\infty} \frac{dp}{2\pi}\, e^{\mathrm{i}p(x-x')} = \delta(x - x'). \tag{A.13}$$

Let us proceed to demonstrate some properties of this function.

Propriety 1:

$$\delta(x - x') = \delta(x' - x) \tag{A.14}$$

This property immediately follows from Eq. (A.13) by changing the variable $p \to -p$.

Propriety 2:

$$\delta(a(x - x')) = \frac{\delta(x - x')}{|a|} \tag{A.15}$$

This property immediately follows from Eq. (A.13). It can be expressed as

$$\delta(a(x - x')) = \int_{-\infty}^{\infty} \frac{dp}{2\pi}\, e^{\mathrm{i}ap(x-x')} \tag{A.16}$$

We write $a = \frac{a}{|a|}|a| = \mathrm{sign}(a)|a|$ and change the variable to $p' = ap$, so $dp' = adp$. We then have

$$\begin{aligned}\delta(a(x - x')) = \frac{1}{a} \int_{-\mathrm{sign}(a)\infty}^{\mathrm{sign}(a)\infty} \frac{dp'}{2\pi}\, e^{\mathrm{i}p'(x-x')} &= \frac{\mathrm{sign}(a)}{a}\delta(x - x') \\ &= \frac{\delta(x - x')}{|a|}.\end{aligned} \tag{A.17}$$

Propriety 3: Consider a function $f(x)$ that vanishes at points x_m, i.e., $f(x_m) = 0$. Then:

$$\delta(f(x)) = \sum_m \frac{\delta(x - x_m)}{|f'(x_m)|} \tag{A.18}$$

where $f'(x_m)$ is the first derivative of the function f evaluated at x_m.

This property follows from the fact that $\delta(f(x))$ is nonzero only if x is equal to one of the points x_m. In the vicinity of one of these points, we can then approximate $f(x) = f'(x_m)(x - x_m)$ and rewrite

$$\delta(f(x)) = \sum_m \delta(f'(x_m)(x - x_m)) \tag{A.19}$$

Property 3 is now a direct consequence of Property 2.

Appendix B
Levi-Civita Tensor: Definition and Properties

The Levi-Civita tensor ε_{ijk} is a three-index object where each index can take the integer values 1, 2, and 3. Therefore, in total, we have 3^3 possible combinations such as $\varepsilon_{111}, \varepsilon_{112}, \varepsilon_{113}, \varepsilon_{121}, \varepsilon_{122}, \varepsilon_{123}$, etc. The value of ε_{ijk} can be 0, 1, or -1 according to the following rule

$$\varepsilon_{ijk} = \begin{cases} 0 \text{ if two or more indices are equal} \\ 1 \text{ if } (i, j, k) \text{ is an even permutation of } (1, 2, 3) \\ -1 \text{ if } (i, j, k) \text{ is an odd permutation of } (1, 2, 3) \end{cases} \tag{B.1}$$

The Levi-Civita tensor is particularly useful for compactly expressing the components of the cross product between two vectors. Let us consider the vector $\mathbf{c} = \mathbf{a} \times \mathbf{b}$. The components of $\mathbf{c}$ are then:

$$c_1 = a_2 b_3 - a_3 b_2, \qquad c_2 = -a_1 b_3 + a_3 b_1, \qquad c_3 = a_1 b_2 - a_2 b_1 \ . \tag{B.2}$$

Let us show that these three components can be expressed in a compact form as

$$c_i = \sum_{jk} \varepsilon_{ijk} a_j b_k \ . \tag{B.3}$$

For example, for the first component

$$c_1 = \sum_{jk} \varepsilon_{1jk} a_j b_k \ . \tag{B.4}$$

Since ε_{ijk} is zero if two or more indices are equal, the only non-zero contributions occur when $(j, k) = (2, 3)$ or $(j, k) = (3, 2)$. Therefore

$$c_1 = \varepsilon_{123} a_2 b_3 + \varepsilon_{132} a_3 b_2 \ . \tag{B.5}$$

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Now, $(1, 2, 3)$ is an even permutation of $(1, 2, 3)$, while $(1, 3, 2)$ is an odd permutation of $(1, 2, 3)$. Therefore, $\varepsilon_{123} = 1$ and $\varepsilon_{132} = -1$. Substituting these values, we obtain the first equation in Eq. (B.2). Similarly, for the other components, we have

$$c_2 = \sum_{jk} \varepsilon_{2jk} a_j b_k = \varepsilon_{213} a_1 b_3 + \varepsilon_{231} a_3 b_1 = -a_1 b_3 + a_3 b_1 \tag{B.6}$$

$$c_3 = \sum_{jk} \varepsilon_{3jk} a_j b_k = \varepsilon_{312} a_1 b_2 + \varepsilon_{321} a_2 b_1 = a_1 b_2 - a_2 b_1 \tag{B.7}$$

Below are some properties of the Levi-Civita tensor that allow us to easily perform calculations involving vector products

Propriety 1: If $a_{jk} = a_{kj}$ then

$$\sum_{jk} \varepsilon_{ijk} a_{jk} = 0. \tag{B.8}$$

This property, used to derive Eq. (2.41), can easily be demonstrated. From the definition in Eq. (B.1), it follows that exchanging j with k results in $\varepsilon_{ijk} = -\varepsilon_{ikj}$. Therefore

$$\sum_{jk} \varepsilon_{ijk} a_{jk} = -\sum_{jk} \varepsilon_{ikj} a_{jk}. \tag{B.9}$$

Since j and k are dummy indices, we can rename j with k and k with j on the right-hand side, obtaining:

$$\sum_{jk} \varepsilon_{ijk} a_{jk} = -\sum_{jk} \varepsilon_{ijk} a_{kj} = -\sum_{jk} \varepsilon_{ijk} a_{jk}. \tag{B.10}$$

In the last step, we used the fact that $a_{jk} = a_{kj}$. Therefore, the sum in question is equal to minus itself. Since zero is the only number equal to minus itself, the sum is zero.

Propriety 2:

$$\sum_{k} \varepsilon_{ijk} \varepsilon_{pqk} = \delta_{ip}\delta_{jq} - \delta_{iq}\delta_{jp}. \tag{B.11}$$

This property has been used to derive Eq. (4.60). The proof is quite simple. Fixing the pair (i, j), if $i = j$, then $\varepsilon_{ijk} = 0$, and we obtain $0 = 0$ since the right-hand side is also zero. If $i \neq j$, then there exists only one k for which $\varepsilon_{ijk} \neq 0$. For that k to make ε_{pqk} different from zero, the pair (p, q) must be equal to either the pair (i, j) or the pair (j, i). In the first case, i.e., $p = i$ and $q = j$, the only term in the sum is $(\varepsilon_{ijk})^2 = 1$, while in the second case, i.e., $p = j$ and $q = i$, the only term in the sum is $\varepsilon_{ijk}\varepsilon_{jik} = -1$. In both cases, the right-hand side coincides with the left-hand side, and therefore, the property is demonstrated.

Propriety 3:

$$\sum_{jk} \varepsilon_{ijk}\varepsilon_{pjk} = 2\delta_{ip} \tag{B.12}$$

We have used this property to derive Eq. (4.59). The proof follows directly from Eq. (B.11) by setting $q = j$ and then summing over j:

$$\sum_{jk} \varepsilon_{ijk}\varepsilon_{pjk} = \sum_{j} \left(\delta_{ip}\delta_{jj} - \delta_{ij}\delta_{jp}\right) = 3\delta_{ip} - \delta_{ip} = 2\delta_{ip} \tag{B.13}$$

Appendix C
Euler's Gamma: Definition and Properties

The Euler Gamma function is defined by the formula:

$$\Gamma(z) = \int_0^\infty dt\, t^{z-1} e^{-t}. \tag{C.1}$$

For small t, the value of $e^{-t} \approx 1$, and therefore, the primitive of the integrand behaves like t^z/z. It follows that if $\Re[z] < 0$, the integral diverges. Hence, Eq. (C.1) provides a representation of the analytic function $\Gamma(z)$ only for $\Re[z] > 0$. This function is of particular interest because

$$\Gamma(z+1) = \int_0^\infty dt\, t^z e^{-t} = -t^z e^{-t}\Big|_0^\infty + \int_0^\infty dt\, z t^{z-1} e^{-t} = z\Gamma(z). \tag{C.2}$$

It follows that for $z = n$

$$\Gamma(n+1) = n\Gamma(n) = n(n-1)\Gamma(n-2) = \ldots = n!\,\Gamma(1). \tag{C.3}$$

Now

$$\Gamma(1) = \int_0^\infty dt e^{-t} = 1, \tag{C.4}$$

and hence

$$\Gamma(n+1) = n!. \tag{C.5}$$

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